DOCTOR OF PHILOSOPHY

Pyrolysis of contaminated energy crops and the characterisation of the gained biochar

Zsuzsa Mayer

2013

Aston University

PYROLYSIS OF CONTAMINATED ENERGY CROPS AND THE CHARACTERISATION OF THE GAINED BIOCHAR

ZSUZSA AJSA MAYER

Doctor of Philosophy

ASTON UNIVERSITY

June, 2012

Summary

The simultaneous use of willow as a vegetation filter and an energy crop can respond both to the increasing energy demand and to the problem of the soil and water contamination. Its characteristics guarantee that the resources are used economically. As a vegetation filter, willow uptakes organic and inorganic contaminants. As a fast growing energy crop it meets the requirements of rural areas without the exploitation of existing forestry.

The aim of the research was to gather knowledge on the thermal behaviour of willow, uptaking contaminants and then used as an energy crop. For this reason pyrolysis experiments were performed in two different scales. In analytical scale metal-contaminated wood was investigated and bench scale pyrolysis experiments were performed with nitrogen-enriched willow, originated from a wastewater treatment plant.

Results of the pyrolysis showed that 51-81 % of the wastewater derived nitrogen of willow was captured in the char product. Char had low surface area (1.4 to 5.4 m^2/g), low bulk density (0.15–0.18 g/cm^3), high pH values (7.8–9.4) and high water-holding capacity (1.8 to 4.3 cm^3/g) while the bioavailability of char nutrients was low. Links were also established between the pyrolysis temperature and the product properties for maximising the biochar provided benefits for soil applications.

Results also showed that the metal binding capacity of wood varied from one metal ion to another, char yield increased and levoglucosan yield decreased in their presence. While char yield was mainly affected by the concentration of the metal ions, levoglucosan yield was more dependent on the type of the ionic species.

Combustion experiments were also carried out with metal-enriched char. The burnout temperatures, estimated ignition indices and the conversion indicate that the metal ions type and not the amount were the determining factors during the combustion.

Results presented in the Thesis provide better understanding on the thermal behaviour of nitrogen-enriched and metal contaminated biomass which is crucial to design effective pyrolysis units and combustors. These findings are relevant for pyrolysis experiments, where the goal is to yield char for energetic or soil applications.

Keywords

Contaminated biomass; Char combustion; Metals in wood; Nitrogen cycle; Wastewater treatment

Acknowledgement

I would like to express my sincere gratitude to my supervisor, Professor Andreas Hornung for giving me the opportunity to join the European Bioenergy Research Institute (EBRI) in 2009 and for being open to my independent and individual initiatives and procedures in research. During these three years under his supervision I had the privilege to participate in the establishment of the EBRI analytical laboratory from the very beginning, to be involved in teaching activities of the University and to supervise the final year project of six master students working with our group.

I am very thankful to Dr. Andreas Apfelbacher for his assistance throughout my research project and to Dr. Philip Davies for the financial support via Science Bridge (EP/G039992/1), the initiative of the Research Councils (RCUK) and Department of Science and Technology (DST).

Professor Vasudevan (Indian Institute of Technology, Delhi), Professor Toky (Haryana Agricultural University, Hisar), Professor Sen (Indian Institute of Technology, Delhi), Professor Srivastava (G.B. Pant University, Pantnagar), Drusilla Riddel-Black (Lupus Science), Chris Johnston (Rural Generation) have my sincere thanks for organising my visits to the energy crop plantation fields and to the wastewater treatment plants around India and UK.

Special thanks are due to Dr. Alistair McCracken (Agri-Food & Biosciences Institute, Belfast), David Bielawski, Bob Massingham and Brian Johnson (Environmental Protection Department, St Helens Council) for providing the wood material we used during our experimental work.

Very special thanks to Dr. James Titiloye, Dr. Daniel Nowakowski and Dr. Mike Perry (Aston University) for providing advice in areas of expertise.

I wish to thank Richard Collins and Anne Nuttall (Coventry University) for their guidance with ICP–OES measurements and to Dr. Elisabeth Schröder (Karlsruher Institute of Technology) and Dr. Baogui Shi (Aston University) for the surface area and XPS measurements. I wish to thank Neeranuch Phusunti, Katharina Kebelmann, Josephine Mmojieje and Surila Darbar too for their technical support in lab. I would also like to express my appreciation to all other staff members and fellow PhD students of EBRI and BERG for their support.

Finally I would like to give my special thanks to my parents for the constant moral support and to Andras Rac who, as a professional editor, helped to form all my published works.

Table of Contents

List of Tables

List of Figures

List of Schemes

List of Abbreviations

ASTM	American Society for Testing and Materials
BET	Brunauer–Emmet–Teller method
BOD	Biological Oxygen Demand
BOT	Burnout Temperature
CHP	Combined Heat and Power
C_{total}	Total Conversion
DI	Deionised (water)
DSC	Differential Scanning Calorimeter
DTG	Differential thermogram
EGA	Evolved Gas Analysis
FT–IR	Fourier Transform–Infrared Spectroscopy
GC	Gas Chromatography
GC–MS	Gas Chromatography–Mass Spectrometry
GWP	Global Warming Potential
HHV	Higher Heating Value
HTT	Highest Treatment Temperature
ID	Inner Diameter
ICP–OES	Inductively Coupled Plasma–Optical Emission Spectroscopy
LHV	Lower Heating Value
MS	Mass Spectrometry
PID	Proportional–Integral–Derivative controller
Py–GC–MS	Pyrolysis–Gas Chromatography–Mass Spectrometry
Py–MS	Pyrolysis–Mass Spectrometry
TDS	Total Dissolved Solid
TG	Thermogravimetry
TGA	Thermogravimetric Analysis
TG–MS	Thermogravimetric Analysis–Mass Spectrometry
TIC	Total Ion Curve
TN	Total Nitrogen
XPS	X-ray Photoelectron Spectroscopy
WI	Wastewater Irrigation
wt %	Weight percentage

Nomenclature

Biochar and biomass char Despite of the similarity, historical definitions distinguish *biochar* from *biomass char*, also known as charcoal. While the latter has been produced and used as heating fuel for centuries, the former belongs to a new concept of soil management and carbon sequestration.

For this reason the present Thesis uses the term 'biochar' in **Part I** where the char analysis and characterisation were primarily based on soil quality related measurements. The term 'biomass char' is used in **Part II**, where the solid product of pyrolysis was characterised as a potential energy source throughout combustion experiments. Other names like *black carbon*, *dark earth*, *Terra Preta* or *agrichar* can be also found in literature [1-3] but were not used in the thesis.

Bio-oil and pyrolysis liquids During the last few decades the liquid product of pyrolysis has also been referred to many synonyms. Throughout this Thesis, the terms *pyrolysis liquid* or *bio-oil* will be used.

Wastewater and wastewater irrigation Throughout the present Thesis the term *wastewater* will either refer to treated wastewater (effluent) or untreated (raw) wastewater. Wastewater irrigation can refer to flood irrigation, spray irrigation, subsurface drains and other similar applications.

Chapter 1: Introduction and the Outline of the Thesis

1.1. A Waste-to-Energy Concept

Ever growing population increases its energy demand and the organic and inorganic waste. This burden on the eco-system and puts pressure on research groups, therefore it has never been more desired to provide a solution for both the energetic and environment remediation issues simultaneously.

Conventional biofuels like ethanol and biodiesel are both available and renewable energy sources. However, these sugar-, starch- and vegetable oil-based first-generation fuels, jeopardise the security of food supply by conquering valuable agriculture lands [4].

Unlike the above mentioned food crops, energy crops, like wood do not compromise provision supply. Wood is also a renewable energy source which has been used since the beginning of the human history [5]. Its applications have hardly changed if we consider combustion as an ancient energy conversion technology and pyrolysis which has been used for for thousands of years, originally to provide charcoal and lately for bio-oil production [6].

Pyrolysis is the thermal degradation of the biomass in inert atmosphere which can provide a renewable liquid fuel as its primary product. Bio-oil (or pyrolysis liquid) is the subject of intense research and investigations for direct energy applications with highest efficiency [7]. Bio-oil therefore represents a second generation biofuel which does not compromise food crop security.

Waste management technologies have also progressed. Several of them can effectively reduce the harmful effects of waste, on the expense of very drastic chemical processes. Despite the achievements of the chemical technologies, the 21st century is returning to the less drastic biological methods which are primarily based on the ability of nature to remediate itself [8]. Bioremediation does not require physical or chemical intervention as plants can capture inorganic or organic contaminants. Vegetation filters are cultivated to uptake organic contaminants from wastewater, while plants cultivated for phytoremediation can accumulate and immobilise heavy metals or other inorganic soil contaminants.

Remediation by plants is an available and exciting technology to solve environment issues. Its application overlaps with the solution of cultivating energy crops. The disadvantage of the process is the elevated level of contaminants in the crops itself.

The combustion of waste and contaminated biomass in traditional boilers is a widely applied, well-documented and also well-controlled technology. Meanwhile our knowledge about the fate and effects of contaminants during pyrolysis is lagging behind.

1.2. Problem Background and Motivation

During my PhD research I had the great opportunity to participate in the Science Bridge Project, which is the collaboration of Aston University and the Indian Institute of Technology Delhi – along with other UK and India based institutes. This project was established to maximise the efficiency of the conversion of wasteland, wastewater and agricultural waste into renewable fuel.

As my background is soil remediation and the primary focus of my research group at Aston University is biomass pyrolysis, my research goal was to combine the two approaches: using contaminated biomass from remediation as pyrolysis feedstock and introducing it into the waste-to-energy process.

After visiting several plantations and wastewater treatment plants in India, working with colleagues from several universities (G.B. Pant University of Agriculture & Technology in Pantnagar, Haryana Agricultural University in Palwal etc) and analysing local energy crops like *Melia azadarach*, *Pongamia*, *Alstonia scholaris*, *Eucalyptus tereticornus* and *Ailanthus excels*, we had to come to a conclusion that it would be very difficult – or even impossible – to ship suitable wood material from India to the UK for this project. For this reason we sought contaminated biomass, preferably short rotation energy crops from universities, research institutes and councils across the UK and Europe. Besides our new resources we insisted on keeping the original concept (pyrolysis of contaminated wood from wastewater/land treatment plants).

We got two positive answers: one from the Agri-Food & Biosciences Institute, Belfast, where the willow plantations have been irrigated with farm wastewater and another one from the Environmental Protection Department of St Helens Council, where a metal contaminated playground has been planted with a wide range of short rotation crops – e.g. with willow. We gained permission to collect samples from both sites and started a new set of analyses with these new samples. While the early tests with wastewater irrigated biomass gave promising results, the biomass from St Helens did not show significant concentration of contaminants – therefore the metal contaminated willow had to be replaced with willow prepared under laboratory conditions.

1.3. Outline of the Thesis

The present research investigates the pyrolysis behaviour of wastewater irrigated wood, rich in organic nitrogen (in bench scale) and metal contaminated wood, prepared under laboratory conditions (in analytical scale). The Thesis also discusses the two possible applications of the pyrolysis derived char associated with the pyrolysis of metal and nitrogen enriched wood (see also Figure 1). Based on the two different types of contaminants and application approaches, the Thesis is divided into two sections:

Part I: Pyrolysis of wastewater irrigated energy crops and biochar characterisation for soil applications

Nitrogen, in a similar way to carbon, has a complex and fragile global cycle. Anthropogenic activities from the beginning of the 20th century have interfered with this fine nitrogen balance by capturing N_2 from the atmosphere for fertiliser production [9].

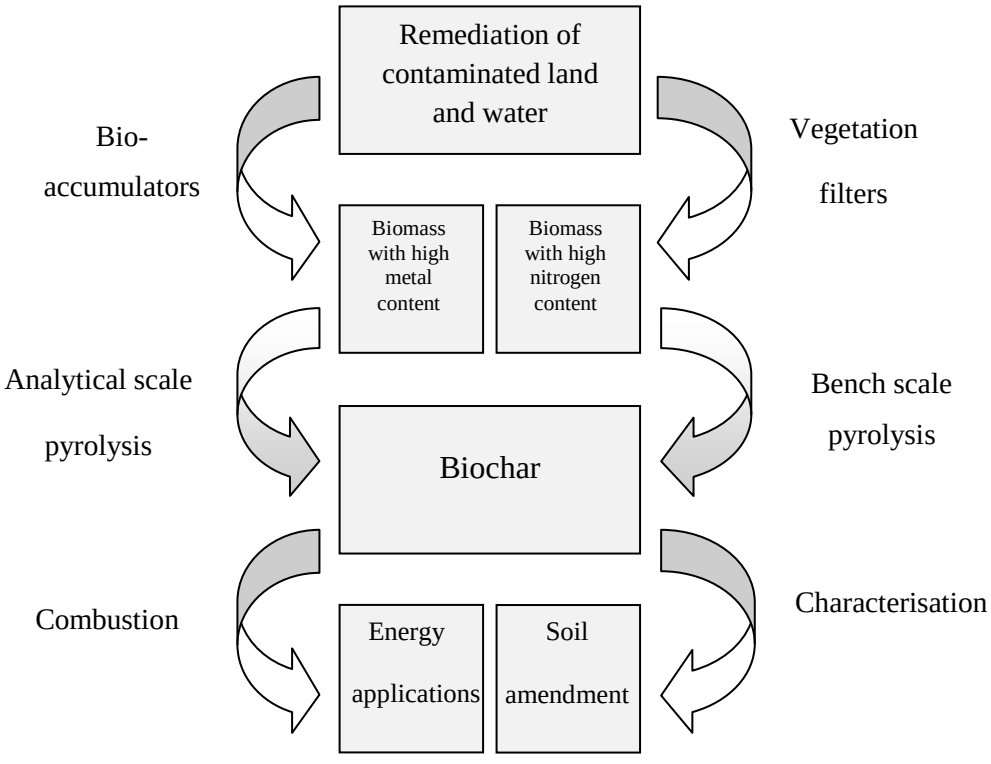


Figure 1 General scheme showing biomass pyrolysis and conversion to energy and to soil amendment

When this stable nitrogen from the atmosphere enters the forage crop production and the livestock raising cycle, it returns to the environment in more reactive forms. During the combustion of energy crops the fuel-bound nitrogen forms greenhouse gases which are liberated to the atmosphere, therefore both fertiliser applications and biomass combustion are directly related to environmental problems (see also Chapter 2: Background of Part I).

Short-rotation plantations irrigated with effluent have both high nitrogen uptake capacity [10] and enhanced growing characteristics. The latter applies without fertilisers or fresh water usage [11, 12]. Furthermore, wastewater irrigation reduces the cost of wastewater treatment while crops cultivated on the land can provide solution for the increasing biomass and energy demand of rural areas without destroying existing forestry [11]. In order to choose appropriate feedstock and design a biomass-to-energy conversion technology both the economical and environmental aspect of a project should be considered.

The objective of **Part I** was to place energy crops into the global nitrogen cycle by following biomass-bound nitrogen from wastewater irrigation via energy conversion to the products of pyrolysis. Therefore **Part I** focuses on waste related environmental issues and soil management.

The Thesis also aims to investigate the properties and possible applications of contaminated wood derived biochar. Biochar, which is the solid co-product of pyrolysis, is mainly made of carbon and the ash content of the pyrolysed biomass. Char carbon has the potential of long-term sequestration in soil. Biomass pyrolysis with soil applications of the biochar has a negative greenhouse gas (GHG) emission – with a CO_2 *equivalent* ranging from few hundred kilograms up to a few tonnes of $CO_2\ eq\ t^{-1}$ *dry biomass* – with a positive net energy [13-15].

Engineering biochar is a new concept for maximising the benefits for soil applications. A comprehensive char characterisation is the first step to design char and to assess its suitability to the different type of soils, therefore **Part I** provides an in-depth physicochemical characterisation of the feedstock and pyrolysis products and focuses on properties relevant to water and soil quality. For this reason the pyrolysis experiments were mainly performed in bench scale (gram scale) and products were analysed by GC–MS, XPS and FT–IR techniques.

Part II: Wood pyrolysis and char combustion in the presence of inorganic contaminants

Another source of environmental pollution is metal contamination in soil. Pyrolysis of hyperaccumulators (plants which uptake and accumulate metals from soil) is the focus of **Part II**. Even though it is a common practice to produce synthetic hyperaccumulators under laboratory conditions [16] there is no one single and generally accepted preparation method for them. For

this reason **Part II** first compares the most common metal addition methods then analyses the pyrolysis behaviour of synthetic bioaccumulators in the presence of different metals.

Biomass char is a valuable energy source with properties similar to charcoal. Due to its high fixed carbon content biochar is also a renewable energy source with a heating value up to 30-35 MJ/kg [17]. Biomass char has higher energy density and better combustibility properties than traditional biomass, and higher reactivity than coal due to its oxygen content [18] and its incoherent carbon structure [19]. As the soil applications of char derived from the pyrolysis of contaminated wood would return metals to the environment, the objective of **Part II** was to approach char production with the possibility of energy applications. **Part II** also analyses the degradation processes and fuel qualities of biomass and biomass derived char in the presence of metal contaminants. The thermal degradation processes (pyrolysis and combustion) were investigated in analytical scale (milligram scale) by TGA, TG–MS, Py–MS and Py–GC–MS techniques.

As different analytical techniques were applied in **Part I** and **II**, both parts contain a detailed description of the used materials and the applied methods. The Thesis ends with a conclusion section and with suggestions for further works.

Part I: Pyrolysis of Wastewater Irrigated Energy Crops and Biochar Characterisation for Soil Applications

Chapter 2: Background of Part I[1]

The following chapter reviews the nitrogen cycle of effluent-irrigated energy crop plantations, starting from waste water treatment to thermo-chemical conversion processes. It also highlights the advantages of biochar as a soil amendment.

2.1. Wastewater and Wastewater Treatments

2.1.1. Nitrogen in Municipal Wastewater

Nitrogen in domestic wastewater is present in both inorganic and organic forms. Organic nitrogen from human diet and metabolism is transformed into free ammonia (NH_3) and ammonium cation (NH_4^+) by microorganism [20, 21]. The NH_3 to NH_4^+ ratio in water is depending on the temperature and the pH of the water. The presence of free NH_3 above the concentration of 0.002 mg/L is toxic for the ecosystem [22]. Ammonia is also the source of inorganic nitrate and nitrite (NO_3^-, NO_2^-) nitrogen in wastewater [21]. Inorganic nitrogen is an essential plant nutrient, however, high concentrations in water cause *eutrophication*, an extreme bloom in the population of plants with an enhanced growth period followed by the necrosis of the biomass. The degradation of dead plant tissues increases the oxygen demand of fresh water, therefore, eutrophication leads to oxygen scarcity and decreased self-cleaning ability of the biomass system [23]. The presence of nitrate and nitrite anions in drinking water causes cyanotic conditions like shortness of breath, methemoglobinemia and blue-baby syndrome [24, 25]. To protect human health and aquatic life the nitrogenous contaminants of wastewater must be controlled. Table 1 contains some requirements set up by different governments and the typical nitrogen values in different types of wastewater.

Table 1 Typical nitrogen values and requirements in water and wastewater

	Nitrogen forms	**Concentration** (mg N/L)	**Source**
Typical nitrogen concentration in *grey wastewater*	TN[a]	0.6–74	[26]
Typical nitrogen concentrations in domestic *raw wastewater*	TN	20–80	[26]
Requirement of the European Council for urban *wastewater* treatment	TN	10	[27]
Primary standards of the *National Primary Drinking Water Regulations* by US EPA[b]	Nitrate-N	10	[28]
Health value of the *Australian Drinking Water Guidelines*	Nitrate-N	11.3	[29]

[a] TN: Total Nitrogen; Sum of organic nitrogen, ammoniacal nitrogen, nitrate-nitrogen and nitrite-nitrogen
[b] EPA: Environmental Protection Agency, U.S.

[1]Chapter based on: Mayer Z A, Apfelbacher A, Hornung A (2011) Journal of Scientific and Industrial Research 70: 675-682.

2.1.2. Biological Wastewater Treatment

The physicochemical removal of nitrogen from wastewater is possible, however, biological methods have proved to be more effective and less expensive treatments [30].

The biological removal of nitrogen is based on the mixed populations of live bacteria naturally present in wastewater which are able to convert nitrogen compounds to other chemical forms.

The *activated sludge* formed by these living microorganisms is the core of modern industrial wastewater treatment technologies. This mineralisation process (consecutive steps of *ammonification*, *nitrification* and *denitrification)* of the wastewater-derived organic matter provides oxygen, nitrogen and energy for the bacteria to produce new cells [31]. To ensure the most suitable environmental conditions for the microorganisms (e.g. aerobic zone for nitrification and anoxic zone for denitrification) several industrial processes have been designed like the *Bio-Denitro process*, modified *Ludzack-Ettinger process*, *Bardenpho process*, etc. [30].

When these conventional wastewater treatment facilities are not available – mostly in developing countries – stabilisation ponds (Figure 2) are the most widely used municipal wastewater treatment systems [32]. Even if the climate favours microbial activity these stabilization ponds cannot reduce the concentration of nitrogen satisfactorily [33].

Figure 2 A stabilisation pond in Rajasthan, India.

The pond receives local, untreated wastewater from Surajgarh (population: 25,000) and the cleaning process is based on uncontrolled biological activities.

2.1.3. Vegetation Filters

If the high cost of the commercial technologies discounts the use of sufficient wastewater treatment, the unregulated or poorly regulated water turns to a potential risk factor to human health and environment [34, 35]. To eliminate this risk it is crucial to reduce the concentration of nitrogen and other pollutants before any effluent reaches the environment.

The application of biological filter systems like *soil* and *vegetation filters* represents an alternative on-site wastewater treatment (Figure 3). While the first pilot tests were carried out by major firms to treat cannery effluents, the treatment of municipal water receives more and more attention now in developing countries [36, 37]. This type of wastewater management is able to reduce the concentration of organic and inorganic contaminants in the water and remove 73–97 % of the total nitrogen content [38]. This low-cost treatment also assimilates nitrogen as plant nutrients back into the environment while pathogens from the wastewater cannot compete with the natural microbial population of the soil [39, 40].

Figure 3 Vegetation filters cultivated for wastewater treatment

a) Drain system carrying untreated gray water from the campus of the G.B. Pant University, Pantnagar into the river close to Uttarakhand, India. **b**) Flood irrigated vegetation filters (*melia*, *poplar*, *willow* and *eucalyptus*) polishing the grey water at the same university campus

2.2. Nitrogen, the Essential Plant Nutrient

The role of soil in the biological-cycle is to store and supply nitrogen and other essential nutrients for plants. The average amount of organic nitrogen in soil is 3300 kg/ha, however, the available nitrogen for plants is less than 1 % of the above amount as vegetations are not able to uptake any kind of forms of soil nitrogen [41].

The synthesis of plant cell components (e.g. amino acids, nucleic acids, enzymes, chlorophyll etc.) is unachievable without nitrogen; nitrogen deficiency in plants causes slow growth which can be recognized by the pale green colour of the leaves. Without available nitrogen there are no processes in plants [41]. For the formation of new cells, plants uptake nitrogen – along with water – in the form of NH_4^+ or NO_3^- during their growing period (*assimilation*) or store extra nitrogen (*immobilisation*) [42].

Nitrogen is being absorbed from soil during the whole life of the plants but the nitrogen use efficiency of plants varies according to the stage of maturity, seasons, environmental conditions of the site and the fertility status of the soil as well [41, 43]. The latter factor is particularly important in terms of crop yield as nitrogen supply is a main limitation factor to plant growth [44].

If the nitrogen supply within the soil is not sufficient, land productivity can be improved by organic and inorganic (also known as synthetic) macronutrient plant fertilisers. The most widely used synthetic fertilisers are ammonia-based products [45]. The source of nitrogen in these fertilisers is the atmosphere containing molecular nitrogen in 78 %. The direct reaction of molecular nitrogen and molecular hydrogen to NH_3 is the base of the widely applied *Haber-Bosch process* [46] which provides more than 140 million tonnes of ammonia to farmers around the world every year [47].

The Haber-Bosch process and the modern soil fertility management of the 20th century have made a significant contribution to the growth of Earth's population which has almost quadrupled since 1900s. To sustain this growing population industry produces millions of tons of fertiliser and this production is responsible for more than 1 % of the world's energy consumption. Since hydrocarbon combustion is the main energy source of ammonia production, the fertiliser industry is a major contributor to greenhouse gas emission too [48]. In addition to energy consumed in production, transportation of the fertilisers also contributes to the world's greenhouse gas emission with 37 teragrams CO_2-eq per year [49]. There is also an estimated 2.5–4.5 Tg N emitted from the nitrogen-fertilised soil to the atmosphere each year [50].

When the cost or availability of the technology does not make it possible to apply inorganic fertilisers, alternative – and possibly more sustainable – nitrogen sources should be considered to increase the productivity of agricultural land.

Similar to inorganic fertilisers, wastewater is a source of supplemental nitrogen. According to studies, nitrogen uptake of rain-fed eucalyptus in New Zealand is in the range of 30-80 kg/ha/year while the uptake in effluent-irrigated plantations can be one magnitude higher [10]. Research results have also proved that plants have enhanced growing characteristics as a result of excess nitrogen from

wastewater, grey water or effluents [51-53]. Plants can polish water by absorbing organic contaminants for their growth. The absorbed nitrogen nutrients from water are converted to amino acids and stored in wood [54] or transferred from roots to shoots for protein synthesis [55].

2.3. Energy from Biomass

Treating contaminated water by vegetation filters requires fast-growing plants, like willow [56]. Willow is also a widely cultivated fuelwood for energy applications.

Willow and other short-rotation plants represent a cheap and renewable energy source with high energy potential, given as their heating (or calorific) value. The higher heating value (HHV) is the energy available from the fuel and it is generally given in units of energy per unit of weight (cal/g; J/g or Btu/lb). Table 2 contains some typical heating values of fuelwood and other solid fuels.

Figure 4 shows a wastewater irrigated energy crop plantation. The plots belong to the bioremediation project of the Agri-Food & Biosciences Institute (N. Ireland), where the harvested willow is chipped and locally combusted in traditional boilers for heat production.

Table 2 Heating values of energy crops, charcoals and fossil fuels

		HHV (MJ/kg)[a]	**Source**
Fuelwood			
	Softwood (average)	20.0	[57]
	Hardwood (average)	18.8	[57]
	Straw (maize silage)	20.0	[58]
Charcoals			
	Charcoal from rice husk	17–18	[59]
	“High quality” charcoal	28–33	[6]
Fossil fuels			
	General purpose coal	32–42	[60]
	Petrol	45–47	[60]

[a:] dry basis

a) Irrigation system and water tank with nitrogen-rich farm wastewater

b) Wastewater irrigated willow plantation in its second year

c) Woodchip drying and storing facility

Figure 4 Wastewater treatment combined with energy crop cultivation in Hillsborough, Northern Ireland

Even though charcoal represents lower energy value than fossil fuels, its combustion can turn to a CO_2 neutral energy conversion technology. The combustion of fuelwood can also be CO_2 neutral, however, combustion converts fuel-nitrogen to nitric oxides (NOx = NO + NO_2) and nitrous oxide (N_2O) [61-66] which are contributors to acid rain formation [67]. N_2O is also a greenhouse gas with a *global warming potential* (GWP) of 289 (over 20 years) where one unit represents the global warming potential of CO_2 [68]. The emission of NOx contributes to acidification and it also causes eutrophication and ground-level ozone formation [69].

Increased nitrogen content in the biomass also means increased emission of NOx during combustion [70]. The estimated emission of NOx from biomass combustion was 5-5.9 TgN in 2000 [50] and based on the fact that the energy demand and the biomass fuel consumption are increasing [71], this NOx emission must be even more significant now and need to be decreased drastically.

To control the harmful effects of combustion plants' pollutants, organisations like Environmental Protection Agency of the United States or the Intergovernmental Panel on Climate Change have elaborated their guidelines and emission criteria [72, 73]. The most common way to fulfil these regulations is the application of flue gas cleaning systems (primary reduction with excess air, secondary catalytic reduction, etc.) but these technologies add cost, particularly in small bioenergy facilities [70]. Another effective way to reduce the environmental impact of biomass-derived NOx pollution is the application of alternative energy conversion technologies with better emission characteristics.

2.4. Biomass Pyrolysis

Pyrolysis is a thermochemical process where the biomass is being converted into more dense energy sources. During biomass pyrolysis processes the macromolecules and biopolymers undergo a thermal degradation in the absence of oxygen, which leads to liquid (bio-oil), solid (biochar) and gaseous products.

In terms of nitrogen oxide emission, pyrolysis is a more desirable energy conversion technology than combustion; while biomass combustion releases fuel-nitrogen in the form of NOx and N_2O, the inert atmosphere and high temperature of pyrolysis does not favour the formation of oxidised pollutants [74].

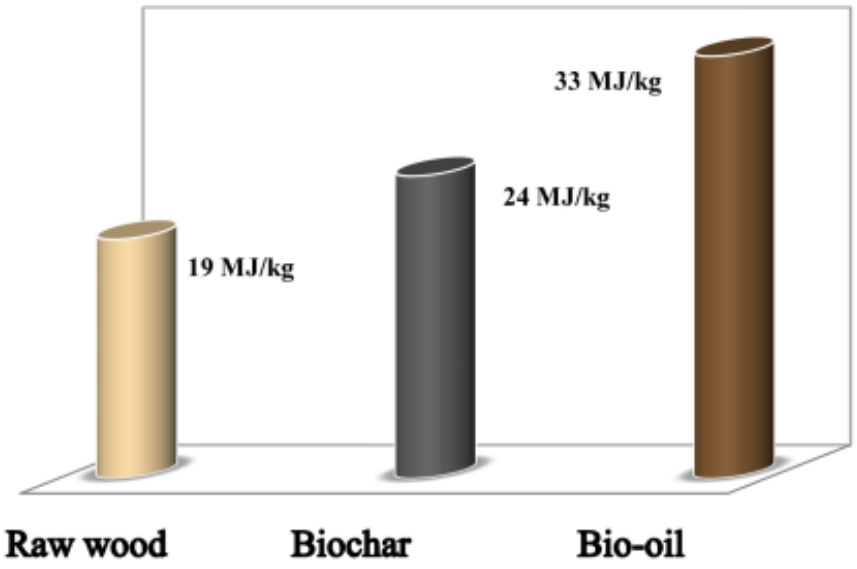


Figure 5 Typical energy content of untreated willow and its solid and liquid pyrolysis products

(Raw material: 100 g chipped willow pyrolysed in a fixed bed reactor. Pyrolysis temperature: 460 ºC, purging gas: N_2, see also Chapter 3)

Pyrolysis also has the ability to generate highly energetic bio-oil which represents most of the energy content of the biomass (Figure 5) with the additional benefit that it can be easily pumped or transported when wood is used as a pyrolysis feedstock.

Bio-oil is a relatively new energy source and its energy applications are still developing, but its combustion in boilers, turbines and engines has been successfully used for heat and electricity production [75, 76]. Table 3 contains some typical (thermal and electrical) power output values from different bio-oil applications.

Table 3 Power outputs from bio-oil combustion

Hot water generation	
Boiler fuelled with pyrolysis oil (BTG Biomass Technology Group BV, The Netherlands)	150 kW
Electric power generation	
Pyrolysis liquid combustion in diesel engine (VTT Energy, Finland)	84 kW
Pyrolysis liquid combustion in diesel engine (Wärtsilä Diesel International, Taiwan)	1.5 MW
Pyrolysis liquid combustion in gas turbine (University of Rostock, Germany)	75 kW
Combined heat and power generation (CHP)	
Pyrolysis liquid combustion in a Stirling CHP unit (ZSW, Germany)	10-25 kW_{th}, 4-9 kW_e [a]

[a:] W_{th}: Thermal power output, W_e: Electrical power output**.** Source: Czernik, 2004 [7]

2.5. Biochar as a Soil Amendment

Besides of the energetic applications of the bio-oil, the most widely acknowledged benefit of pyrolysis products is the long-term carbon sequestration potential of biochar when returned to soil [13, 77].

Biochar is also known for the ability to contribute to soil properties by changing its physical and chemical characteristics but the contribution of biochar to soil quality factors can be both positive and negative [78, 79].

While biochar characterisation as a solid fuel follows well established standards (like proximate and ultimate analyses and heating value measurements [80]), biochar characterisation as a soil amendment still lacks these kind of standards [81]. Biochar characterisation should therefore follow soil quality analysis methods and determine factors like: bulk density, which affects the pore size distribution of soil and the conditions for gas exchange [82]; porosity, which affects the water-holding capacity of soil and the surface area – a shelter for microorganism [83]; functional groups on surface which determine the cation exchange capacity of the char and the nutrient retention in soil [84]; total dissolved solids, which give an estimation on the amount of the mobile charged ions migrating from char to soil [81] and pH, which also has impact on the mobility of ions and affects soil microbial activity [85]. Besides these physical and chemical properties, the nutrient recovery from biochar for plants can be another focus of the characterisation processes [86].

The most important physicochemical properties of biochar are directly related to the type of the biomass used for char production and to the applied temperature of pyrolysis [6, 80, 83]. By selecting the right feedstock, finding the right pyrolysis temperature and elaborately characterising the physicochemical properties, char can be safely applied to soil as an amendment. Furthermore, it is possible to produce engineered biochar with the designed properties to remediate specific soil issues, which opens the doors to a new type of soil management [79, 87].

Chapter 3: Experimental of Part I[2]

The following chapter describes pyrolysis feedstock, the set-up of the bench scale pyrolysis experiments and the methods used for the characterisation of wood and the gained pyrolysis products.

3.1. Materials

Willow (*Salix*) was cultivated in monoplots in the framework of the bioremediation programme of Agri-Food & Biosciences Institute (ABFI, Hillsborough, N. Ireland) and was harvested in September 2010. The plantations were irrigated with farm wastewater, which had low pH (5.7) and was rich in organic matter (BOD: 2650 mg/l) and nitrogen (100 mg N/l) and willow trees were in their second year of re-growth after coppicing. Samples were also collected from an un-irrigated control plantation.

The harvested wood was chipped without leaf parts and pre-dried at 60 °C for 48 h. Gross samples and laboratory samples were prepared from the pre-dried wood material according to the ASTM E 954 – 94 and D 6323 – 98 standards [88, 89] (see also Appendix I). For biomass characterisation and pyrolysis experiments the laboratory samples were dried on 105 °C and were grinded to a homogeneous powder with particles < 1 mm.

3.2. Pyrolysis Set-up

Bench scale pyrolysis was performed in an in-house constructed fixed bed reactor, which was designed and built in the frame of the present project and Thesis (Figure 6). The

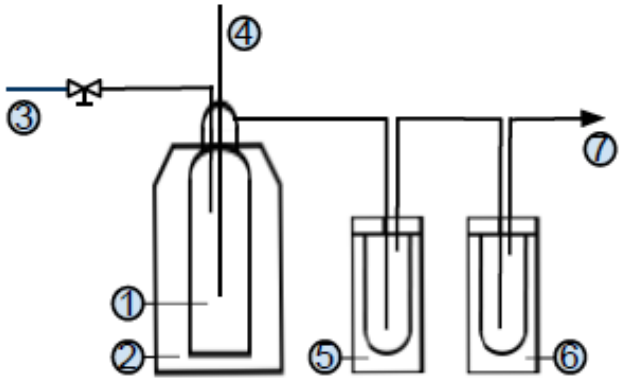


Figure 6 Equipment set-up of bench scale pyrolysis

1) Quarts tube (Length: 400 mm, ID: 80 mm); **2**) Electrically heated furnace; **3**) Inlet of the purging gas; **4**) Thermocouple of the temperature controlling unit; **5**) and **6**) Cold traps with liquid N_2; **7**) Outlet of the non-condensable gases

[2] Chapter based on: Mayer Z A, Eltom Y, Stennett D, Schröder E, Apfelbacher A, Hornung A: Characterisation of Engineered Biochar for Soil Management. Submitted to the Environmental Progress & Sustainable Energy (Paper under review. Manuscript number: EP-12-086)

quartz work tube with 100 g of biomass was placed inside the electrically heated vertical split tube furnace coupled with a PID temperature controller (both from Carbolite Ltd.). The thermocouple of the temperature controller unit was located directly in the centre of the bed. To establish the desired pyrolysis conditions, nitrogen purging gas was applied at the top of the working tube through a gas inlet with a flow rate of 50 cm^3/min. The pyrolysis vapours were driven off through an insulated outlet and condensed in cold traps submerged into liquid nitrogen. Temperature has the highest impact on biochar structure and properties [6, 83], therefore the highest treatment temperature of pyrolysis was varied between 410 °C and 810 °C, while the heating rate was kept approximately at 30 °C/min during each pyrolysis experiments.

The mixture of reaction water and condensable vapours (bio-oil) was collected and weighed in the cold traps. The char residue was left in the reaction chamber and allowed to cool to room temperature then it was collected and kept in sealed plastic bags in dark before analyses. The gas yield was calculated from char and bio-oil yields as a difference. Repeated runs were also conducted with identical set-ups and the pyrolysis experiments were also repeated under helium atmosphere to check repeatability and ensure that nitrogen adsorption on surface did not cause any overestimation of nitrogen content during the char analysis.

3.3. Wood and Product Characterisation

3.3.1. Bio-oil Analysis by GC–MS

After completing the bench scale pyrolysis experiments, both liquid and solid products were subjected to further analysis. Pyrolysis liquid was first separated into water and organic phases then the organic phase was dissolved in ethanol and the water phase was extracted with acetone. The chemical composition of both phases were characterised by gas chromatography–mass spectrometry (GC–MS, model: HP 5890). The injection unit temperature of the GC was 310 °C and it was coupled to a DB–1701 column (60 m × 0.25 mm, 25 μm). The GC oven was heated from 40 °C to 295 °C at a rate of 3 °C/min while the system was purged with helium carrier gas with a split ratio of 20. Separated compounds were recorded with the HP 5972 mass selective detector with ionisation energy of 70 eV and a scanning range of m/z 50-500 in the full scan mode.

Bio-oil is a complex mixture of several organic compounds. After separating and recording these compounds by gas chromatography–mass spectrometry, their identification can be based on the measured retention times or on the fragmentation pathways within the ion source of the detector. The main problem with the retention time-based compound identification is that retention time depends on the applied GC method (column type and length, carrier gas type and flow rate, heating profile etc.) therefore the recorded time is not comparable with the retention times from other methods, laboratories or instruments [90]. The limitation factor of mass spectrometry based identification is that

different molecules can have very similar fragments which often results in misidentification of the oil compounds.

Based on the linear relationship between the retention time and the number of carbon atoms within the molecule the recorded retention times were converted to Kováts retention indices [90, 91]

$$I = (100n) + (100z) \cdot \left(\frac{t_R(unknown) - t_R(n)}{t_R(N) - t_R(n)} \right)$$

where

I: Kováts retention index for temperature programmed chromatography

n: the number of carbon atoms in the smaller alkane,

N: the number of carbon atoms in the larger alkane,

z: the difference of the number of carbon atoms in the smaller and larger alkane,

t_R: the retention time

and a mixture of diesel oil and lubrication oil (BAM-K010, purchased from the Federal Institute for Materials Research and Testing) used as a reference material. The calculated retention indices were therefore independent from the applied GC method and could be used more accurately for compound identification.

A "two-dimensional" GC–MS search algorithm was also established with a MassFinder 3 software package (from Hochmuth Scientific Consulting, Germany) and used for the bio-oil analysis. The advantage of the "two-dimensional" search algorithm is that it enabled the compound identification by using both the measured MS data and the calculated retention indices simultaneously. This new "two-dimensional" search algorithm provided more reliable compound identification than the two methods separately.

3.3.2. Proximate, Ultimate and Amino Acid Analyses

Ash content is an approximate measure of the mineral content and other inorganic matter in samples. The ash content in wood and biochar was determined according to the ASTM E 1755-01 method [92]. This test method covers the determination of ash, expressed as the mass percent of residue remaining after dry oxidation at 575 °C.

Approximately 0.5 - 1.0 g of grinded and pre-dried wood was weighted into tared crucibles then the crucibles were placed in the muffle furnace and ignited at 575 °C until all the carbon was eliminated. The crucibles were let to cool to room temperature and weighted again. From the final weights the ash mass percents were calculated as the sample's 105 °C dried mass. Porcelain ashing crucibles, a Carbolite muffle furnace (575 ± 25°C) and an HR-120 analytical balance (sensitive to 0.1 mg) were used during the procedure.

The elemental composition analysis of the samples (C, H and N) was carried out by an external laboratory (Medac Ltd, Chobham, UK). The applied quantitative flash combustion method was based on the instantaneous oxidation of the wood samples in a Carlo-Erba 1108 Elemental Analyzer. First few mg of samples were placed in tin capsules and dropped into the vertical quartz reactor tube (1000 °C) and burnt in an excess of oxygen. The combustion products (CO_2, H_2O etc.) were separated on a chromatographic column and detected by a thermal conductivity detector. Oxygen contents were calculated by difference.

The amino acid composition of wood was determined by an external laboratory (Alta Bioscience, Birmingham, UK). The ion exchange separation of the amino acids followed by post column ninhydrin colourimetric detection. This amino acid analysis is a quantitative analytical technique which accurately measures the protein content and of the wood samples.

The sample preparation is an extension of our routine amino acid extraction and protein precipitation using trichloracetic acid: About 20 g of wood material was ground to a fine "sawdust" like powder using a motorised mortar grinder at maximum pressure. Approximately 10 g of this was weighed accurately into a 100 ml volumetric flask. The material was solvated with 2.5 % trichloracetic acid until fully wetted and any gas production had ceased, then the volume was adjusted. The flask was sonicated for 10 minutes with intermittent shaking, the sample was then mixed thoroughly by shaking and inverting repeatedly. A sample of about 12 ml was taken and centrifuged at 10000 rpm for 5 minutes to separate the insoluble materials. 200 µl of the supernatant was analysed using an increasing pH gradient of lithium citrate buffers for amino acid separation

AltaBioscience uses instruments based on Waters Alliance HPLC systems which are validated for linearity and reproducibility. Samples were processed as a batch alongside a set of pre-mixed commercial and freshly prepared calibrants. Both samples were processed in an identical manner, and analysed during a single run, to obtain the most accurate comparison.

All results are reported in dry matter basis.

3.3.3. Thermogravimetric Analyses of Wood and Wood Components

The wood and the pure wood-forming compounds (hemicellulose from birchwood, purchased from Sigma-Aldrich in form of xylan; organosolv lignin from BFH-Institute for Wood Chemistry (Germany) and cellulose purchased from Whatman in filter paper form) were pyrolysed in a Mettler TGA/DSC 1 Star System. Approximately 10 mg sample was heated up from room temperature to 105 °C and kept isothermal for 10 minutes to remove moisture. Consecutively the samples were heated up to 900 °C with a heating rate of 20 °C/min. The flow rate of the helium purging gas was kept at 50 cm^3/min during all measurements. The recorded weight loss curves were converted to derivative weight loss curves marked as 'weigh loss rate' in Figure 10.

3.3.4. Carbon and Nitrogen Functionalities in Wood and Biochar

C and N functional forms in wood and char were analysed by X-ray photoelectron spectroscopy (XPS). XPS spectroscopy involves irradiating a sample with monochromatic X-rays of a characteristic energy. This causes photo electrons to be ejected with a range of energies depending on the element from which they are emitted and the chemical state of that element. The emitted electrons are then collected and by an energy analyser to be sorted by their energies.

From this electron energy identification, XPS provides information on the elements present at a sample surface and their chemical state, giving an indication of the types of compounds present in the surface. XPS gives quantitative information on almost all elements with a detection limit of 0.1 - 0.01 %. Typically XPS examines the surface to a depth of 7 nm.

The C1s and N1s emission peaks were recorded with a Thermofisher ESCALAB 250 spectrometer equipped with a hemispherical sector energy analyser. Monochromatic Al K_α X-ray with excitation energy of 15 KeV and emission current of 6 mA was used throughout the experiments. The analyser pass energy was 20 eV with step size of 0.1 eV and dwell time of 50 ms.

3.3.5. Biochar Characterisation

Basic methods were chosen to determine the physicochemical properties of char and the availability of plant nutrients. Some of these methods are commonly used for soil quality assessments: bulk density was calculated from the weight of 50.0 cm^3 oven-dried and uncompressed char samples. The pH of 10 wt % char-water slurry was measured with a Sartorius PB-11 pH meter. The same slurry was used to determine the water-holding capacity by following the method of Dugan [93].

To determine the soluble mineral content of biochar, 1.0 g char was mixed and stirred with 50.0 cm^3 deionised water. The total dissolved solid (TDS) content of the char-water slurry was

determined regularly with a conductivity based TDS meter (Hanna Instruments, Bedfordshire, UK) on room temperature. After stirring the slurry for 96 h (700 rpm) the biochar was separated in a centrifuge (10,000 rpm) and both the char residues and the filtrates were kept for further analysis.

Besides of nitrogen, the basic plant elements for crop growth are phosphorus (P), potassium (K), magnesium (Mg) and calcium (Ca). The chemical analysis of biochar can reveal the absolute amount of these elements and the total nutrient content, however, not all these nutrients are extractable and available for plants. The amount of the readily available nutrients and the direct nutrient values of biochar were estimated with Mehlich extraction [94] based soil test kits (HI38082, HI38073 and HI38080) from Hanna Instruments.

The insoluble nutrients of biochar can also become available for crops when they undergo a mineralisation process in the soil. To estimate the amount of the potentially mineralisable nitrogen in biochar, a soil extraction method was followed [95] with some modifications: char residues of the TDS measurements were boiled in 50.0 cm^3 KCl (2M) for approximately 4 hours then separated in a centrifuge (10,000 rpm). Both KCl extracts and water filtrates of TDS measurements were analysed for ammonia (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) with reagent test kits (1.09713, 1.14752, 1.14776 and 1.14942 from Merck Chemicals Ltd, UK) and a Merck Spectroquant Pharo 100 spectrometer.

Prior to surface area measurements the biochar samples were degassed on 220 °C for 12 h. Nitrogen adsorption isotherms were recorded by a NOVA 4000e Surface Area Analyser (Quantachrome) and Brunauer–Emmet–Teller (BET) surface areas were calculated according to the method recommendation of the International Union of Pure and Applied Chemistry (IUPAC) [96]. Measurements and calculations were conducted Karlsruhe Institute of Technology, Germany.

Biochar was also prepared in the Mettler TGA/DSC thermogravimeter (heating rate: 20 °C/min, purging gas: He, 50 cm^3/min) at 100, 200, 300, 400, 500, 600 and 700 °C and the functional groups were analysed by Fourier transform–infrared spectroscopy (FT–IR). For the FT–IR measurements, 2 mg ground wood or char was blended with 200 mg of potassium bromide then the blends were oven dried at 60 °C for 48 h and pressed into pellets. The infrared absorption spectra of these pellets were recorded on a Perkin Elmer Spectrum 100 spectrometer. Four scans per measurements were made in the wavenumber range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Band assignation of the spectra was based on the literature [97-104].

Chapter 4: Results and Discussion of Part I[3]

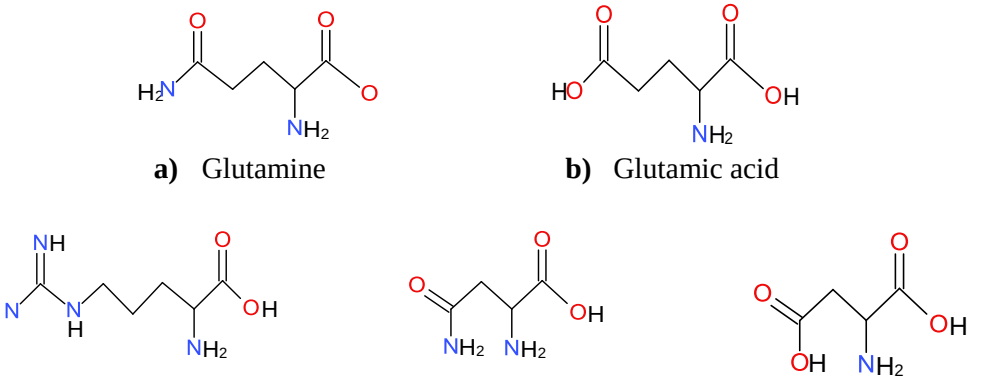
Chapter 4 presents the findings on the analysis of the wood-derived nitrogen, the physical and chemical properties of the biochar produced at different pyrolysis temperatures.

4.1. Nitrogen in Willow

Ultimate analysis revealed approximately twice as much nitrogen in wastewater irrigated willow than in the willow originated from the non-irrigated control plot (0.58 wt % and 0.26 wt %, respectively).

Despite of the low concentrations, this nitrogen enrichment in willow means increased emission of nitric oxides (NOx) and nitrous oxide (N_2O) during the traditional combustion of wood [61-66].

Finding elevated nitrogen content in wood was not unexpected, as wastewater is a source of supplemental ammonium and nitrate nitrogen that plant roots can absorb. The absorbed N nutrients are converted to amino acids and stored in wood [54] or transferred from roots to shoots for protein synthesis [55]. Scheme 1**a-e** shows the main storage and transport amino acids which were present in higher concentration in wastewater irrigated willow (Table 4).



Scheme 1 Main storage and transport amino acids found in willow

Table 4 Free amino acid content of willow from wastewater irrigated (WI) plot and from a control plot

	Arginine (µg / mg)	**Asparagine** (µg / mg)	**Aspartic acid** (µg / mg)	**Glutamine** (µg / mg)	**Glutamic acid** (µg / mg)
Control willow	0.054	0.141	0.066	0.002	0.048
WI willow	0.404	0.177	0.102	0.013	0.103

[3]Chapter partly based on: Mayer Z A, Apfelbacher A, Hornung A in: B. R. Singh, editor. Global Warming (Accepted book chapter, ISBN 979-953-307-820-4) InTech and
Mayer Z A, Eltom Y, Stennett D, Schröder E, Apfelbacher A, Hornung A: Paper submitted to the Environmental Progress & Sustainable Energy (Paper under review. Manuscript number: EP-12-086)

4.2. Mass and Nitrogen Recovery During Pyrolysis

Wood pyrolysis represents an energy conversion method alternative to combustion; pyrolysis results the accumulation of the biomass derived nitrogen in biochar [105], therefore it has the potential to decrease nitrogen liberation from wood.

Increasing the highest treatment temperature (HTT) of pyrolysis increased the liquid and gas yields and decreases char yield (Figure 7). Due to secondary reactions of vapours, liquid yield had a maximum which was followed by a reduction at higher temperatures and the gas yield increases at the expense of biochar yield. This effect of pyrolysis temperature on product distribution is well documented [106, 107], however, the measurements were necessary to determine nitrogen retention in the condense phases [108].

Biochar is a porous material therefore nitrogen uptake from gas-phase could lead to the overestimation of nitrogen retention in the solid phase. Pyrolysis experiments, repeated with N_2 and He purging gas, resulted similar nitrogen content in char residues, which evidenced that there was no nitrogen uptake from the gas phase when reactor was purged with N_2. CHN analysis was conducted with fresh char, therefore it is assumed that the measured char composition was not affected by abiotic uptake of gases during the storage time either.

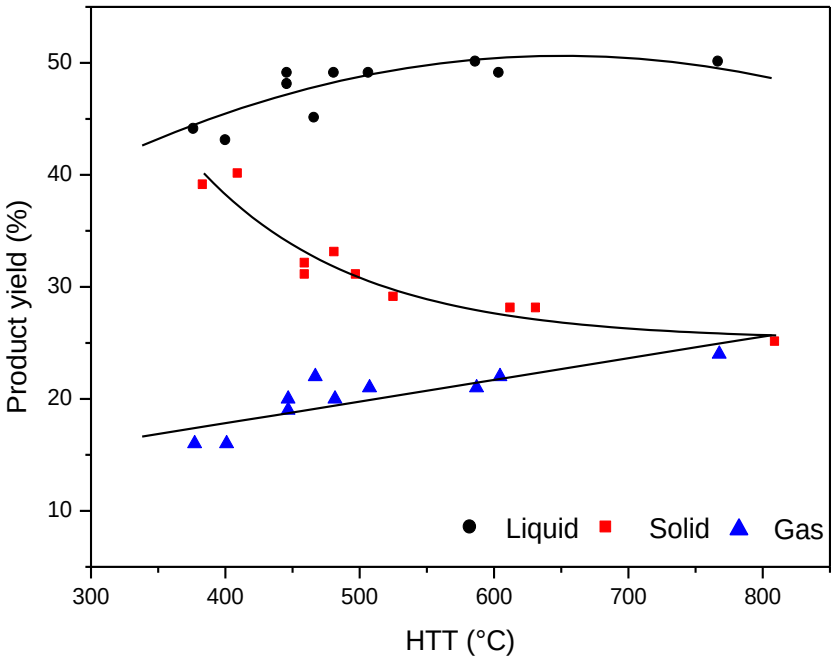


Figure 7 Mass recovery of products of wastewater irrigated willow pyrolysed in bench scale at different temperatures

XPS measurements evidenced that pyrolysis favours the formation of thermally stable nitrogen compounds; the N1s peak fitting of char spectrum indicates the presence of pyrrole/pyridone-N, pyridinium/ammonium-N and pyridine-N with a proportion of 30.5:36.1:33.4 %, respectively (Figure 8). Even though the identification of these peaks is supported by several studies [109, 110], spectrum interpretation in char is difficult due to the similar binding energies of pyrrole and pyridone-N (400.4 and 400.6 eV) or pyridinium and ammonium-N (401.2 and 401.5 eV).

The calculated nitrogen retention in char has a clear decreasing trend: 81 % in char prepared at lowest HTT which gradually decreased to 51 % in biochar, prepared at highest HTT.

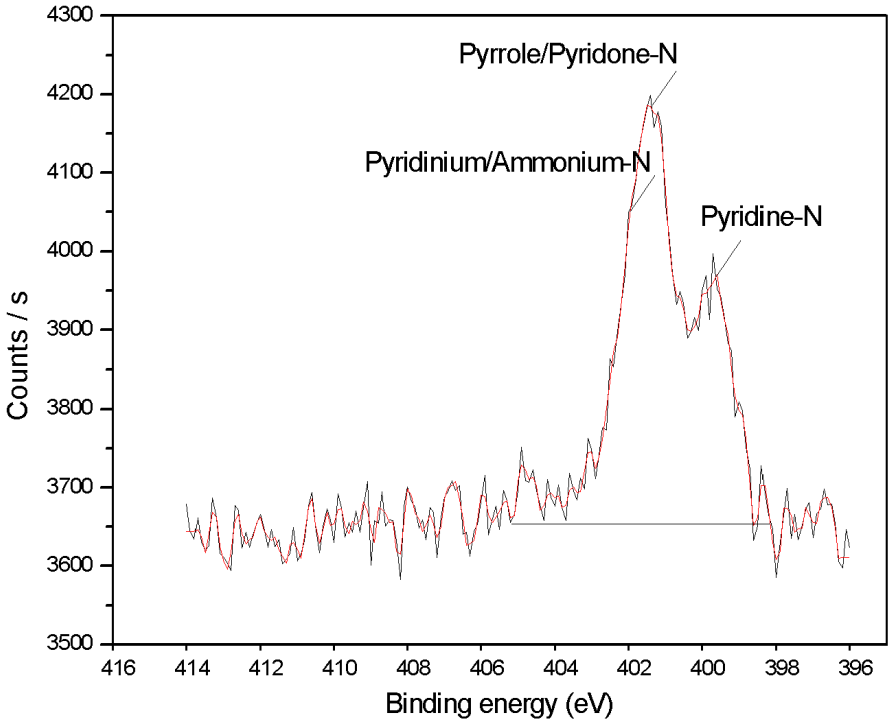


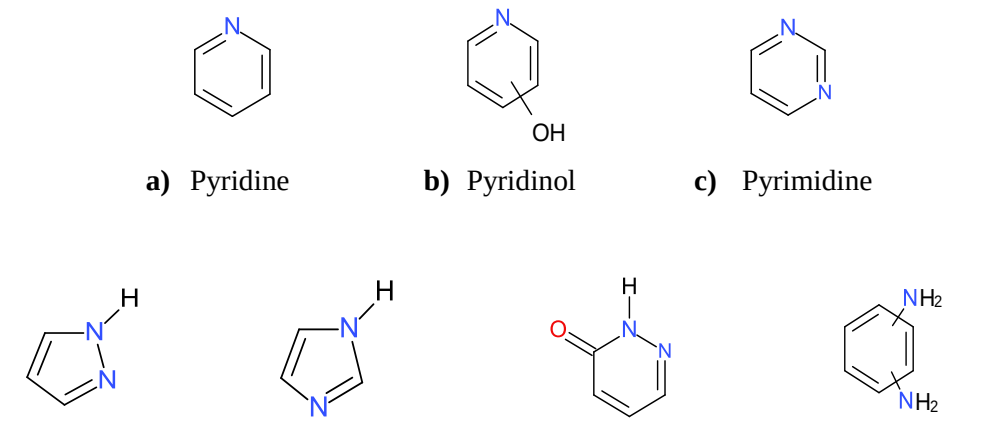
Figure 8 N1s peak fitting for biochar (prepared from wastewater irrigated willow at 470 °C pyrolysis temperature)

Nitrogen in bio-oil also formed stable heterocyclic and aromatic compounds. The compounds identified in bio-oil belong to the chemical families of pyridine, pyridinol, pyrimidine, pyrazole, pyridazinone, imidazole and benzenediamine (Scheme 2**a**-**g**). Nitrogen retention in liquids originated from higher pyrolysis temperatures was more significant and increased from 4.4 % to 15 % in organic phase and from 8.6 % to 28 % in water phase when HTT increased from 410 °C to 810 °C.

4.3. Chemical Composition of the Biochar

Pyrolysis and the volatilisation of the organic compounds lead to the accumulation of the inorganic compounds in char [111]. While both control willow and willow from the irrigated plot had 2.1 % of inorganics (see Appendix II for a more detailed wood characteristics), the ash content of biochar grew from 4.4 % to 6.2 % with increasing HTT.

The release of the volatiles also changed the organic matter structure and caused carbon enrichment in char (see also Table 5). The lowest carbon content was found in char prepared at 410 °C (approximately 700 mg/g) and the highest one was measured in char produced at 810 °C (approximately 820 mg/g). While the former is medium, the latter represents high C content according to the char classification of Joseph et al. [81] which has high importance to estimate the carbon sequestration potential of the pyrolysis residue.



a) Pyridine **b)** Pyridinol **c)** Pyrimidine

d) Pyrazole **e)** Imidazole **f)** Pyridazinone **g)** Benzenediamine

Scheme 2 Nitrogen containing compounds in bio-oil

Carbon enrichment in biochar also changed the O/C and H/C ratios. Figure 9 shows the van Krevelen diagram of the untreated wood (H/C: 0.125, O/C: 0.96) and biochar prepared at different HTT. The O/C and H/C ratios in char decreased with increasing pyrolysis temperature (from 0.32 to 0.1 and from 0.06 to 0.02, respectively) which indicates increasing hydrophobicity [79] and aromaticity [112]. Hydrophobicity and aromaticity play major role in the future stability of biochar [112], therefore the half-life of biochar in soil can be predicted from the measured O/C ratios [113]. The estimated half-life of char prepared under 600 °C is 100-1000 years (O/C: 0.2 – 0.32) and greater than 1000 years in case of char prepared over 600 °C (O/C: 0.1 – 0.2).

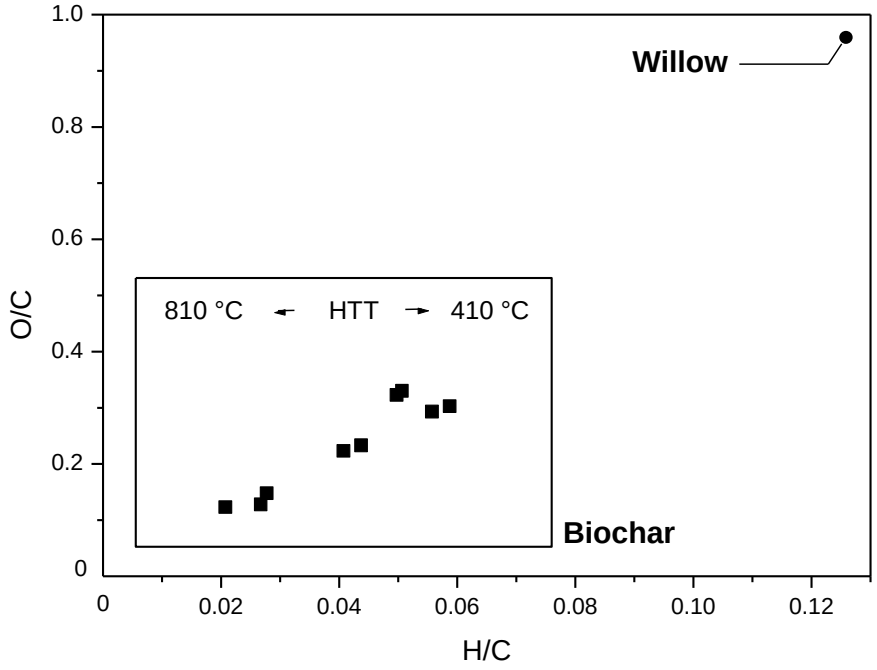


Figure 9 O/C and H/C ratios in wastewater irrigated wood and in biochar

Table 5 Elemental composition of wastewater irrigated willow and biochar, prepared at different pyrolysis temperatures

	C	**H**	**N**	**O**
	Dry matter and ash-free basis, wt %			
Wastewater irrigated willow	47.68	5.98	0.58	45.86
Biochar, 410 °C	73.27	4.32	1.37	21.03
Biochar, 630 °C	85.2	2.44	1.28	11.07
Biochar, 810 °C	87.62	1.85	1.18	9.34

The temperature dependent compositional changes in biochar are directly related to the thermal degradation of the main organic woody biomass compounds, hemicellulose, cellulose and lignin [114, 115]. (For the chemical structure of these compounds see Scheme 3 in Chapter 5 and Scheme 5 and Scheme 6 in Appendix III). The characteristic thermal decomposition temperatures of these compounds can be seen on Figure 10**a-c**. The weight loss curve of willow (Figure 10**d**) can be clearly interpreted as the sum of the independent degradation of the three main organic woody biomass compounds.

The pyrolysis temperature related structural changes and wood conversion to biochar can be seen on the infrared absorption spectra of Figure 11; The first strong broad band between 3700 and 3000 cm^{-1} of dried willow (100 and 200 °C) is the stretching vibrations of O–H functional groups.

In the region of 2975-2840 cm^{-1} the unresolved group of medium weak bands is related to C–H stretching vibrations of CH_n. The peak at 1736 cm^{-1} is assigned to the absorption of free carbonyl groups, therefore it is a typical hemicellulose marker [98, 99]. Bands around 1600

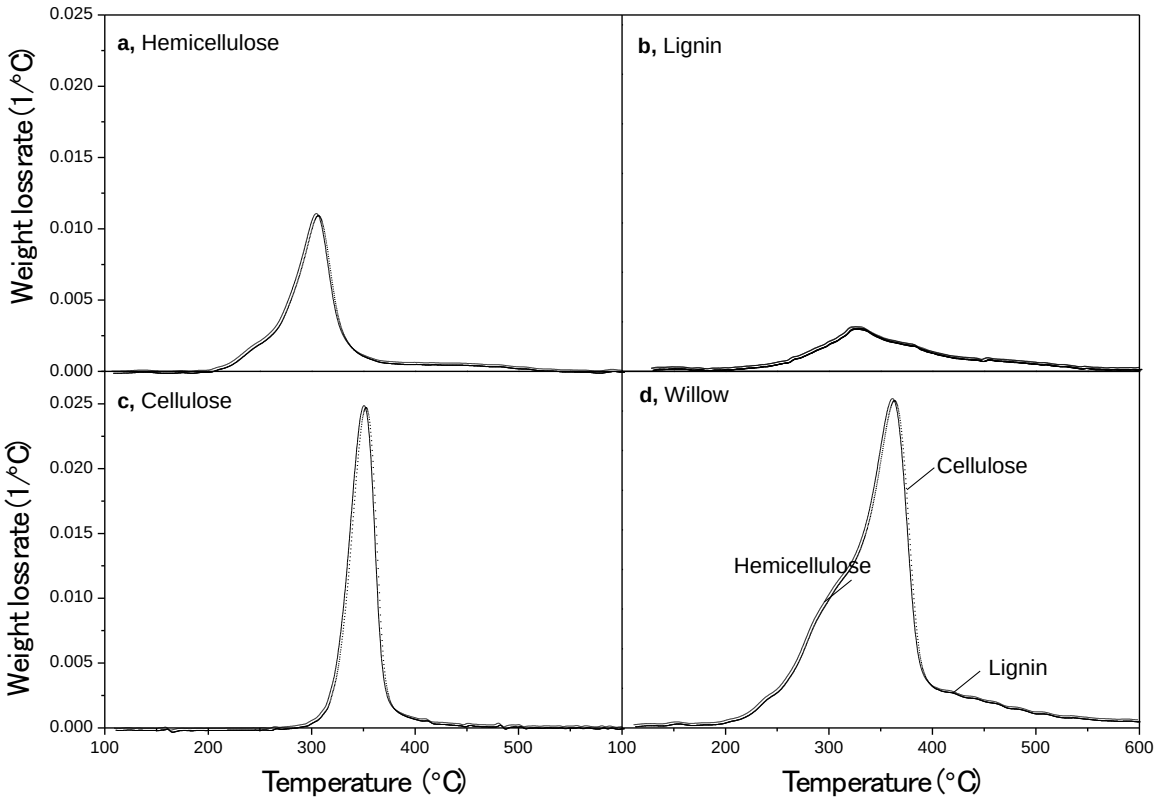


Figure 10 Thermogravimetric analysis of wood and the main wood compounds

a) Hemicellulose (Birchwood xylan); **b**) Organosolv lignin; **c**) Cellulose (filter paper); **d**) Willow

and 1500 cm^{-1} are generally considered as lignin markers as these are the regions of the skeletal vibrations of aromatic rings [103].

Comparing these spectra, it can be seen that the char gradually loses its structural complexity at higher pyrolysis temperatures, as wood carbonisation becomes more completed. Char samples prepared at 300 °C and 400 °C show dramatic decreases in intensity in almost all functional groups; this is the temperature range in which the majority of the pyrolysis mass loss of wood occurs due to the degradation of cellulose, hemicellulose and lignin (see also Figure 10 **a**-**c**). Hemicellulose peak at 1736 cm^{-1} (III) becomes undetectable in char prepared at 400 °C and the O – H (3413 cm^{-1}; I) and CH_n related vibrations (2956, 2924, 2851 cm^{-1}; II) show drastic decreases in char prepared at higher temperatures (400 – 600 °C) where the thermal degradation of cellulose is already completed. Pyrogenic char (prepared at 700 °C or over) has no measured transmittance due to the lack of organic functionalities and the disordered carbon structure.

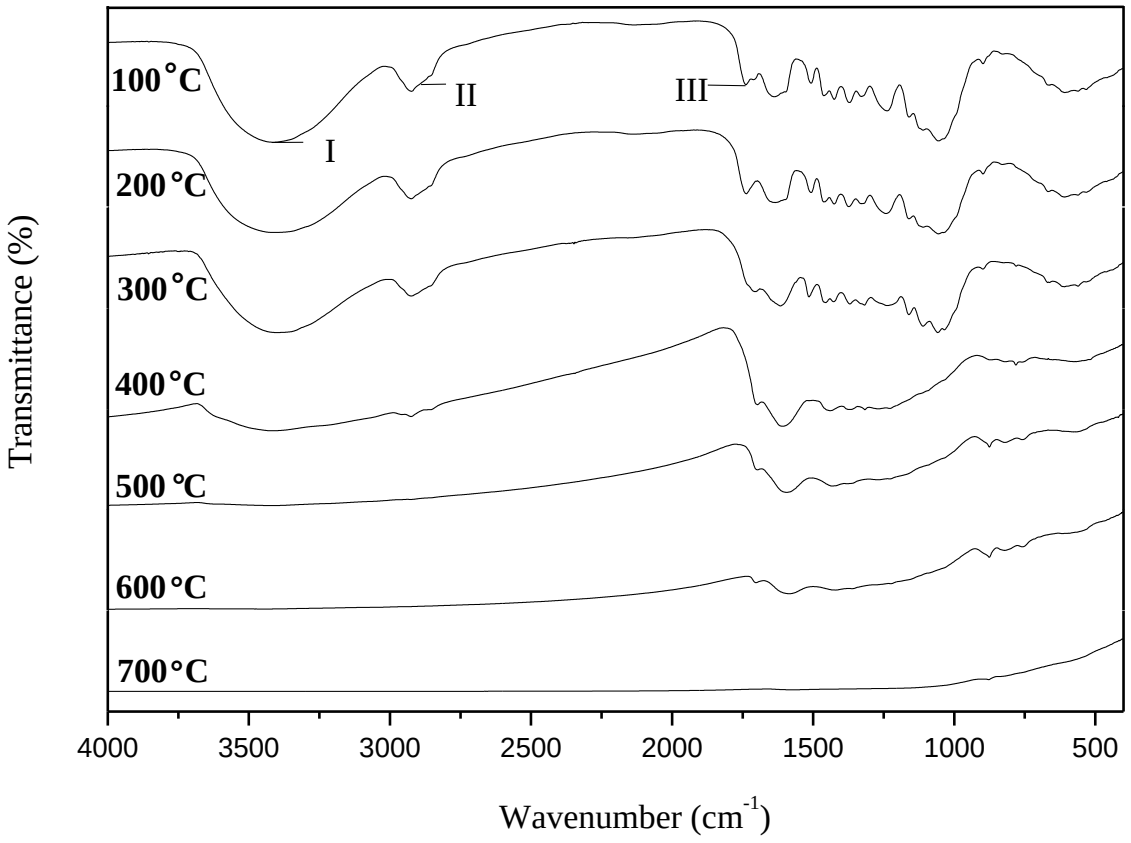


Figure 11 Changes in the infrared spectra of biochar obtained at different pyrolysis temperatures

4.4. Physicochemical Properties of the Biochar

The composition changes observed during wood carbonisation were accompanied by changes in the physical appearance and chemical properties of the biochar; the peak fitting of C1s XPS spectra revealed decrease in C─OH and O─C─O bonding and increase in C─C, C─H and COOH bonding after the pyrolysis of wood (Table 6). XPS measurement is a surface analysis method, therefore the increased proportion of carboxylic acid signals can be the result of abiotic oxidation of methyl functional groups on the biochar surface. The presence of acidic groups on surface is also the reason for the cation exchange property of the biochar [116].

The measured pH value and the density of biochar increased with increasing HTT (Figure 12). Pyrolysis and the thermal degradation of the biomass cause compositional changes in biochar. These temperature dependent compositional changes can be detected by various analytical methods like FT-IR. FT-IR measurement results (Figure 11) suggest that char gradually loses its structural complexity at higher pyrolysis temperatures, as wood carbonisation becomes more completed. Char samples prepared at higher temperatures show dramatic decreases in intensity in OH, COOH etc. functional groups. The lack of these acidic functional

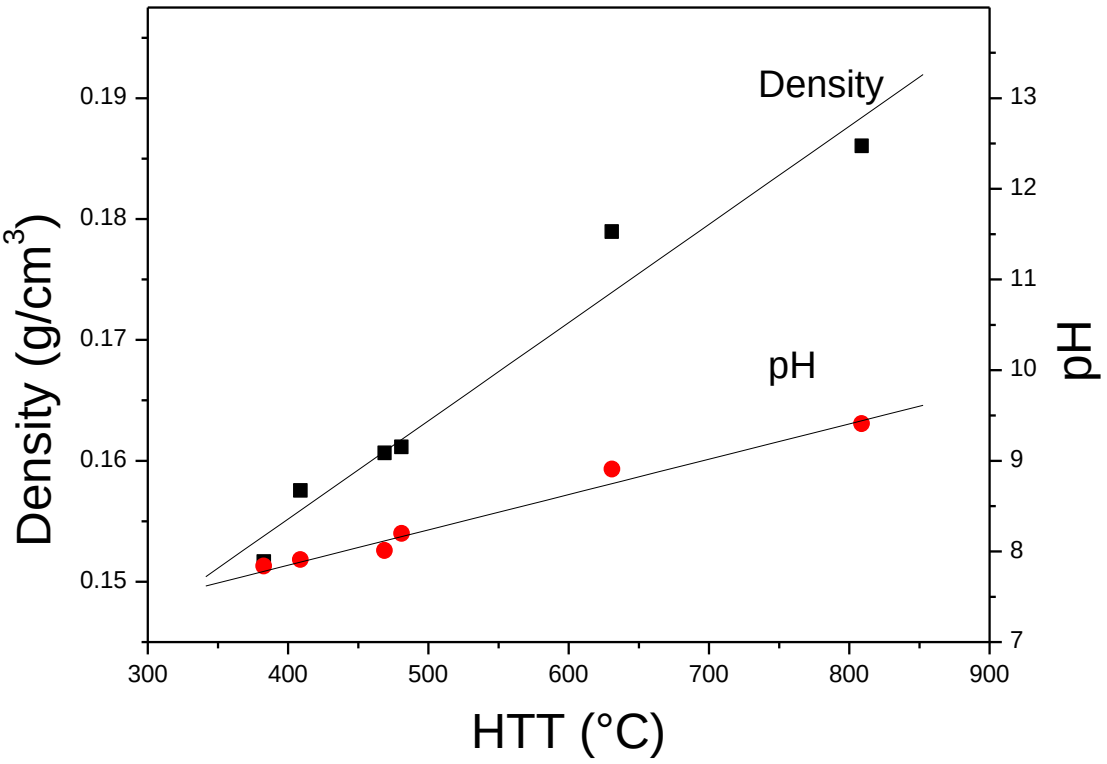


Figure 12 Density and pH of biochar, prepared at different temperatures

groups led to the decreasing pH in biochar prepared at higher temperatures (7.8 - 9.4). This high (alkaline range) pH is favourable for soils affected by acidification.

During the pyrolysis processes both the composition and the complex structure of the wood have changed to form a more homogenous, graphite-like biochar (Figure 11). The loss of volatiles and the formation of the crystallite structure led to the formation of a more organised product with increasing density [83]. Compared to the bulk density of typical medium-textured mineral soils (1.25 g/cm^3) [117]**,** biochar has low density (0.15–0.18 g/cm^3). Lowering soil density by biochar will increase the water-filled pore space, improve relative gas diffusivity and microbial activity [82].

Pyrolysis vapours could develop pores in biochar; however, the small particle size of wood combined with low heating rate allows these volatiles to leave the surface via the natural pores of the material [118]. Very small amount of micropores and mesopores were detected in biochar, which indicates no major morphological changes in solid phase during pyrolysis. The char surface areas were low due to the small pore volumes. When HTT increased from 410 °C to 480 °C the surface area grew from 1.4 to 5.4 m^2/g and the water-holding capacity grew from 1.8 to 4.3 cm^3/g. Both parameters showed mixed results in case of char prepared at higher pyrolysis temperatures.

Table 6 Peak fitting results from XPS measurements

C1s peaks	**C─C / C─H**	**C─OH**	**O─C─O**	**COOH**
Binding energy, eV	285.0	286.6	288.0	289.6
Proportion in willow, %	59.3	25.2	15.3	0.2
Proportion in biochar, [a] %	78.7	13.3	1.5	6.6

[a] Biochar prepared at a pyrolysis temperature of 470 °C

4.5. Nutrient Value of the Biochar

Water extraction of char resulted in quick increase in the concentration of dissolved solids and soluble ions in the first 30 h and reached equilibrium after approximately 96 h (Figure 13). Biochar prepared at higher temperatures gave higher measured TDS values with concentration between 137 ppm (410 °C) and 373 ppm (810 °C), which represent 6.8 and 18.6 mg dissolved material from 1.0 g char, respectively. Char prepared at higher temperature has higher ash content (see also Chapter 4.3.), therefore the increased inorganic/organic ratio of char can explain the increasing TDS concentrations in water.

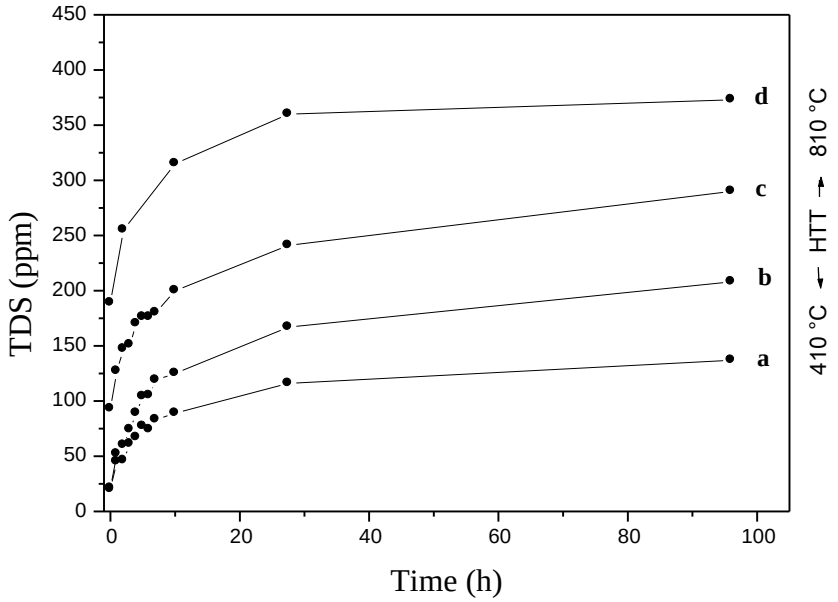


Figure 13 Concentration of the total soluble ions of char

Biochar prepared at pyrolysis temperatures of **a**) 410; **b**) 480; **c**) 630 and **d**) 810 °C

Soil extraction kits gave a quick and comparable estimation of the direct nutrient value of the biochar. The measured P and K concentrations in Mehlich extracts ranged between 28-73 ppm (approximately 0.1-0.3 mg P/g char) and between 15-50 ppm (approximately 0.2-0.4 mg K/g char), respectively. The amount of the exchangeable Ca and Mg in char was between 1.5 to 6 meq/100g (where meq is the milliequivalent of hydrogen). The availability of the measured plant nutrients increased linearly with increasing pyrolysis temperature.

The total nitrogen content in biochar was found between 13 mg/g (HTT: 410 °C) and 11 mg/g (HTT: 810 °C). The calculated C/N ratios of biochar ranged between 52 and 74, which are high values compared to forest soil (C/N ratio: 15-25) or agricultural soil (C/N ratio: 10-13) [119].

XPS results indicated that pyrolysis captures N in heterocyclic ring sstructures, therefore the total N content and the calculated C/N ratios are not necessarily sufficient to estimate the availability of nitrogen from char to plants. The measured concentrations of NH_4^+, NO_3^- and NO_2^- were insignificant both in water and in the KCl extracts, which suggests that this organically bound nitrogen of char is not mineralisable. This is in agreement with the findings of Bridle and Pritchard who reported low bioavailability of char N during soil incubation tests [86]. Stable N forms also indicate that biochar can retain the wastewater and crop derived nitrogen to soil where its long-term sequestration will be realised.

PART II: Wood Pyrolysis and Char Combustion in the Presence of Inorganic Contaminants

Chapter 5: Background of Part II[4]

The following chapter aims to investigate the pyrolysis behaviour of metal-contaminated wood and the properties of the gained products.

5.1. Metal Contaminated Wood

5.1.1. Inorganic Compounds in Biomass

Plants tissues are mixtures of organic compounds and inorganic minerals. These minerals have complex biological functions in plants, however, they are only considered as the ash content of the material when biomass is used for energy purposes.

The most widely known problems associated with ash during the energy conversion technologies are corrosion and metal emission; during large scale fuel combustion the non-combustible mineral content of the biomass forms deposits in the flue gas channels or boilers and damages the gas turbines, to name only a few major problems [120, 121]. Besides these corrosive effects the combustion of metal contaminated biomass can also cause environmental dispersion of toxic trace metals [122, 123].

The pyrolysis of metal contaminated biomass is also receiving more attention, as the number of waste-to-energy projects increases, [124, 125]. Two examples for the increased metal content in pyrolysis feedstock is metal uptake by plants during the remediation of contaminated soil and the decontamination of metal containing effluents with plant parts [126-128].

5.1.2. Investigating the Effect of Inorganic Compounds in Wood

The most common analytical technique used to investigate the pyrolytic behaviour of metal contaminated biomass is thermogravimetric analysis [127, 129-131]. The three main analytical aspects of these investigations are (I) mechanism and kinetics of the biomass degradation, (II) pyrolysis product composition and yield and (III) metal distribution in the pyrolysis product stream [127, 129-131].

Thermogravimetric analysis (TGA) records the mass loss of the heat-treated samples while the mass loss rate (or differential thermogram, DTG) is calculated. While TGA is a technique to follow thermal decomposition of the solid phase, coupled (on-line) analytical methods enable the analysis of pyrolysis products in gas phase too. These evolved gas analysis (EGA) techniques like TG-IR [127, 132], TG-MS [131, 133] or Py-MS and Py-GC-MS [134, 135] are able to track the formation of the condensable and non-condensable organic

[4] Chapter based on: Mayer Z A, Apfelbacher A, Hornung A (2012) Journal of Analytical and Applied Pyrolysis 94: 170-176. and
Mayer Z A, Apfelbacher A, Hornung A (2012) Journal of Analytical and Applied Pyrolysis 96: 196-202.

compounds, while surface ionisation technique can be used to detect the released metal species [121, 136].

Despite of the similarities in the applied analytical methods, there are several contradictions in the literature concerning the effect of metals, especially on biomass degradation temperature [129, 131, 137] or on pyrolysis product yields [129, 138-141]. A possible source of these contradictions is that the samples investigated in these studies were either synthetic biomass (mixture of pure cellulose, hemicellulose and lignin [137, 139]), demineralised biomass [107, 135, 142] or biomass with added metal salts [131, 132, 137, 143]. While samples, prepared with added minerals can provide information on the effect of selected metals, investigations with the previous two biomass types can prevent measuring the effects of the naturally occurring minerals in the raw biomass.

Acid wash is the most common process to remove the inherited mineral matter of the investigated biomass [130, 135, 139, 144] while dry-mixing and impregnation are the general method for metal addition [137, 139-141, 143, 144]. However, both dry-mixing and impregnation raise questions; these common sample preparation methods introduce the metal compounds to the biomass as an inorganic salt, therefore it is difficult to determine if the observed effects on the degradation of the biomass are related to cations of the added metals, to the anions of the metal salts or to the different sample preparation techniques. Therefore, in **Part II** metal ions with two different salt anions were used and three methods for sample preparation were compared before we prepared the metal-added samples for further analysis.

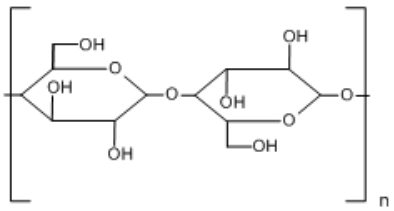
5.1.3. Product Properties and Yields

The solid co-product of the pyrolysis process (biomass char) is a renewable energy source and a valuable heating fuel; due to its high oxygen content and incoherent carbon structure biomass char has higher reactivity than coal [18, 19], higher energy density and better combustibility properties than traditional biomass [145]. Changes in the physicochemical properties of char during combustion has been investigated with a relatively wide variety of analytical tools [19, 146, 147], however, very little is known about the effects of metals during char combustion [148, 149].

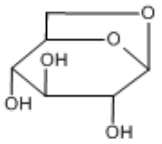
Similar to char, bio-oil is also a valuable product of biomass pyrolysis but not only for energy applications. Levoglucosan (1,6-anhydro-β-D-glucopyranose), and other compounds found in bio-oil, have the additional potential to act as renewable resource for chemicals. Levoglucosan is the anhydrosugar derivative and primary decomposition product of cellulose (Scheme 3 and Scheme 4), therefore a main compound in wood derived bio-oils [150, 151]. Biomass pyrolysis offers the possibility for industrial scale levoglucosan production [138, 152]

for chemical synthesis and fermentation processes [153, 154], however, levoglucosan yield is highly sensitive to the conditions of pyrolysis [153] and to the presence of metals [155].

The objective of **Part II** was to qualify and quantify the influence of different metal cations on wood pyrolysis and to compare levoglucosan yields during the pyrolysis of metal-exchanged wood. A set of combustion experiments were also conducted with pyrolysis-derived char to estimate the effect of inorganic compounds during these energy conversion processes.



Scheme 3 Cellulose polymer



Scheme 4 Levoglucosan

Chapter 6: Experimental of Part II[5]

The following chapter describes the wood biomass used in **Part II** and the different biomass characterisation and metal addition methods. It also contains the description of the performed analytical scale pyrolysis experiments and char combustion experiments.

6.1. Materials

Willow (*Salix*) for the pyrolysis experiments was harvested at St Helens, UK. After removing the leaves the wood material was chipped, pre-dried at 60 °C for 48 h and ground to < 1 mm in a Retsch Knife. For biomass characterisation and demineralisation pre-treatment 0.18-0.85 mm fraction was used (mesh size: 80-20) and dried at 105 °C for 24 h. For metal addition and pyrolysis experiments the same fraction of wood particles was grinded further to gain a more homogeneous powder (mesh size: 100-80, particles: 0.15-0.18 mm).

6.2. Biomass Characterisation

6.2.1. Proximate and Ultimate Analyses

The volatile matter content and ash content measurements require different atmosphere, therefore the flue system of an electric muffle (AAF 1100 from Carbolite) has been modified and adjusted to the British Standards (BS EN 15148: Solid biofuels — Determination of the content of volatile matter and BS EN 14775: Solid biofuels — Determination of ash content) [156, 157]. The fixed carbon content was calculated from the ash and volatile matter contents by difference.

The ultimate analysis (elemental composition analysis) of the samples was carried out by an external laboratory (Medac Ltd, Chobham, UK). The ash residue of the untreated wood (from proximate analysis measurement) was kept for further experiments.

6.2.2. Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is an analytical technique used for the detection of metals in the wood material. ICP-OES uses the plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

[5] Chapter based on: Mayer Z A, Apfelbacher A, Hornung A (2012) Journal of Analytical and Applied Pyrolysis 94: 170-176. and
Mayer Z A, Apfelbacher A, Hornung A (2012) Journal of Analytical and Applied Pyrolysis 96: 196-202.

To determine the mineral content of willow, approximately 0.5 g of samples were wet-digested with 5 ml trace analysis grade nitric acid in a microwave reactor. Samples were made to volume in A grade volumetrics (10 ml) using deionised water and the exact element concentrations of samples were determined by a Perkin Elmer Optima 5300 DV. Multiple standards, prepared using the same digestion method as the sample, were used in order to generate a calibration curve for each element to be determined. The concentration of metal in the sample solution was calculated by running the sample solution against the calibration curve.

Inorganic compounds in demineralised and metal added samples were analysed by the same method.

6.2.3. Wood Fibre Analysis

Besides the ash forming minerals, the main components of wood are the extractives and insoluble fibres, lignin, hemicellulose and cellulose. A gravimetry-based wet chemistry method was used to determine the relative amount of each of these lignocellulosic compounds [158, 159];

Approximately 0.5-1 g of grinded wood was weighted into plastic capsules with pore size of 23 µm. Then a neutral detergent solution (a mixture of lauryl sulphate, sodium sulphite, disodium ethylenediaminetetraacetate, triethylene glycol, disodium phosphate and sodium borate) with a heat-stable alpha amylase (Termamyl), was prepared and used to dissolve the easily-digested proteins in wood, leaving a fibrous residue in the capsules. This residue was primarily cellulose, hemicellulose and lignin.

As a next step hemicellulose content of the wood residue was dissolved in H_2SO_4–cetyl trimethylammonium bromide solution, leaving cellulose–lignin residue in the capsules. This residue was solubilized by 72 % H_2SO_4 leaving a residue made of lignin. After each solubilisation steps the weight of the capsules and samples were measured to calculate the hemicellulose, cellulose and lignin content of wood.

6.2.4. Calorimetry

The heating value (or calorific value) of a sample is the number of heat units liberated by a unit mass of a sample when burned with oxygen in an enclosure of constant volume. In this reaction the sample and the oxygen are initially at the same temperature and the products of

combustion are cooled to within a few degrees of the initial temperature; also the water vapour formed by the combustion is condensed to the liquid state.

Heating value is measured in a bomb calorimeter by measuring the heat liberated by the combustion of all carbon and hydrogen with oxygen to form carbon dioxide and water.

To determine the higher and lower heating values of the raw biomass (HHV and LHV) approximately 1 g of air-dried and grained samples were burned in a Parr 1901 type bomb calorimeter under 450 psi (approximately 3.1 MPa) oxygen pressure and in dynamic method of operation. Thermochemical corrections were applied with fixed values (15 calories for fuse and 10 calories for acid) and benzoic acid was used as a standardizing material.

6.2.5. Fourier Transform–Infrared Spectroscopy (FT–IR)

To identify structural differences in solid phase, 2 mg of ground wood (< 62 μm, mesh size: 250) was oven dried at 105 °C for 12 h, blended with 200 mg of potassium bromide, then pressed into pellets. The infrared absorption spectra of the KBr pellets were recorded on a Perkin Elmer Spectrum 100 FT–IR spectrometer. Four scans per experiments were made in the wavenumber range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Spectra were baseline corrected and normalised to a maximum absorbance of 1.5 for comparison purposes. Band assignation of the spectra was based on the literature [97-103, 160].

See Table 12 and Table 13 in Appendix IV for the complete list of the biomass characterisation methods.

6.3. Sample Preparation

6.3.1. Biomass Demineralisation

To remove the soluble minerals of the wood a common, hydrochloric acid based demineralisation pre-treatment was chosen [161]. After the acid wash, samples were filtered and washed with deionised (DI) water until the effluent was free of chloride. The wood material was dried at 105 °C for 12 h and the ash content, mineral content and other features of the biomass were tested again. Water washed samples were also prepared with the same demineralisation process, where hydrochloric acid was replaced with DI water.

6.3.2. Ion-exchange

Ion-exchanged samples were prepared with the following method: 2 g of demineralised wood material was immersed in 40 ml of 0.1 M metal-nitrate solution and stirred for approximately 100 h at room temperature. Control sample was soaked in DI water and prepared the same way. As a next step samples were filtered, washed with DI water to remove impregnated metals and nitrate anions. This procedure was followed by the immersion of samples in 50 ml deionised water for several days while the conductivity of the water was checked regularly with a manual conductivity meter. When equilibrium had been reached and the conductivity stopped increasing, the wood material was filtered and dried at 105 °C for 12 h.

To compare the ion-exchange behaviour of the pure biomass compounds, the same metal addition process was conducted with organosolv lignin (from BFH-Institute for Wood Chemistry, Germany) and with microcrystalline cellulose powder (purchased from Sigma-Aldrich).

6.3.3. Impregnation and Dry-mixing with Zinc and Lead Sulphate and Nitrate

The metal concentration of the zinc- and lead-exchanged samples were determined with ICP–OES then impregnated and dry-mixed samples were prepared to have the same Zn^{2+} and Pb^{2+} concentrations; 2 g of wood material were immersed in 40 ml in each solution of nitrate and sulphate metal salts. Afterwards the solutions were mixed with a magnetic stirrer until the majority of the water has evaporated. When the impregnation was completed, the wood material was dried in the oven at 105 °C for 24 h.

For dry-mixing, the same amounts of metal salts were mixed and well-homogenised with 2 g of demineralised wood material. Ash added samples were also prepared by dry-mixing demineralised wood with approximately 1.9 wt % of wood ash.

For all metal addition methods analytically pure sulphate and nitrate salts were used (purchased from Sigma-Aldrich).

6.4. Pyrolysis Experiments

6.4.1. Analytical Pyrolysis and Thermogravimetric Analysis (TGA)

Raw, demineralised or metal and ash added wood were pyrolysed in a Mettler TGA/DSC 1 Star System to follow the decomposition processes; 10 mg sample was heated from room temperature up to 105 °C and kept isothermal for 10 minutes to remove moisture. Consecutively the samples were heated up to 900 °C with a heating rate of 20 °C/min. The flow rate of the helium purging gas was kept at 50 cm^3/min during all

measurements. The recorded weight loss curves were converted to derivative weight loss curves marked as ‘rate of weight loss’ (or DTG) in the figures (Figure 15, 18, 19, 20, 21, 23 and 24).

6.4.2. Pyrolysis GC–MS Experiments (Py–GC–MS)

Pyrolysis of wood was also performed in a Py–GC–MS system. The double-shoot pyrolyser (Py-2020iD, Frontier Lab) was coupled to a HP 5972 mass selective detector with a DB-1701 column (60 m × 0.25 mm, 25 μm). The system was purged with He carrier gas with a split ratio of 20.

To analyse the gas phase of pyrolysis products, 0.1-0.2 mg wood was dropped to the 550 °C furnace and vapours were separated on the column while the GC oven was heated from 40 °C to 290 °C at a rate of 3 °C/min. Separated compounds were recorded with an ionisation energy of 70 eV and a scanning range of m/z 20-550 and scanning speed of 1.4 per second.

Pyrolysis products were identified by comparing key fragment ions with NIST 98 Mass Spectral Library and literature data [162]. Yields of gas phase products were estimated by comparing the measured peak areas.

6.4.3. Evolved Gas Analysis by Py–MS

Additional pyrolysis experiments were conducted to analyse the pyrolysis gases and vapours of the pre-treated, untreated and metal added willow. The Py-2020iD double-shoot pyrolyser was coupled to the HP 5972 mass selective detector with an Ultra Alloy-5 EGA column (30 m × 0.25 mm, 25 μm) and the system was purged with He carrier gas with a split ratio of 20. During the measurements 0.1-0.5 mg of sample was heated from 50 °C to 800 °C at a rate of 20 °C/min – similar to the conditions of the TGA measurements – while the GC oven temperature was held on a constant 300 °C. Total ion curves of the evolved gases and vapours were recorded with an ionsation energy of 70 eV, a scanning speed of 1.4 per second and a scanning range of m/z 20-550 with.

6.5. Char Combustion Experiments

6.5.1. Non-isothermal Char Combustion

To determine the burning profile of the char, samples were produced the following way: prior to biomass char production wood samples (raw willow, demineralised willow, willow with added ash and ion-exchanged willow) were fractionated on a 60-mesh screen and char samples were produced at 500 °C in a muffle furnace under N_2 atmosphere.

Biomass char (5.0 mg) was combusted in a Mettler TGA/DSC 1 Star System under a constant airflow of 50 cm^3/min while the temperature increased from 25 to 900 °C with

20 °C/min heating rate. Both weight loss curves and heat flow were recorded and combustion properties of char were estimated by characterisation methods developed for coal and coal-char blends [163-166].

6.5.2. Evolved Gas Analysis by TG–MS

To monitor the gas emission of the combustion experiments, a Pfeiffer QuadStar-200 mass spectrometer was coupled to the thermogravimetric analyser (TG–MS) with an in-house constructed, externally heated coupling system [167]. Key fragment ions were scanned in the range of m/z 2-80 with ionisation energy of 70 eV and 0.24/sec scanning speed.

6.6. Data Analysis

The TGA measurements and pyrolysis experiments of the well homogenised samples gave good and repeatable results and the reported values in Table 8 and Table 9 are the average values of the repeated measurements.

Collected data were also used for general regression analysis; F-test was used to check the relationship between charge and metal binding capacity and then the effect of charges and metal ion concentrations on pyrolysis product yields were scrutinise with Statistica 7.0 software program. As the experiments have not been designed for statistical analysis, these results are only for general observations.

Chapter 7: Results and Discussion of Part II[6]

Chapter 7 compares the different metal addition methods and sample pre-treatments. It also analyses the effects of the added metal ions on the pyrolytic behaviour of wood, on product yields and on the combustion properties of the gained biomass char.

7.1. The Composition of the Untreated and Demineralised Wood

Grinded willow (*Salix*) was chosen to investigate the effect of metals during pyrolysis. The basic characteristics of the raw willow are presented in Table 7. This deciduous wood is not only a local and representative biomass with water polishing potentials but also has proved its ability as bioaccumulator in phytoremediation projects [168, 169].

Prior to demineralisation process the major constituents of inorganic compounds identified in willow were calcium, potassium, magnesium, sodium, zinc and silica with a total ash content of 1.9 wt %. To distinguish between the effects of the inherited and the added metals, the raw biomass was washed with HCl as described in Chapter 6.3.1. This demineralisation pre-treatment removed 99 % of the inherited biomass metals (ash content < 0.01 %), however, when HCl was replaced with DI water the measured ash content remained relatively high (1.3 wt %). Differences between water and acid-based pre-treatments indicate that some of the biomass minerals in willow are in water soluble inorganic salt form while others can resist water treatment but not the acid wash. These metals can be bound to the organic matrix of wood by associating with oxygen-containing functional groups of the biomass polymers like carboxyl groups in cellulose or phenolic groups in lignin [126, 170].

The acid based demineralisation process reduced the concentration of most of the biomass minerals (Ca: 5410/86 ppm; K: 1962/37 ppm; Mg: 330/10 ppm; Na: 188/44 ppm; Zn: 51/15 ppm before and after the pre-treatment, respectively) except Si, which had the same level (28/28 ppm) before and after the acid wash pre-treatment.

Table 7 Basic characteristics of the untreated willow

Relative composition % (dry and ash free basis)		**Ultimate Analysis** % (dry basis)		**Proximate Analysis** % (dry basis)		**Energy Content** (MJ/kg)	
Extractives	7.0	C	48.75	Fixed Carbon	16.7	HHV	19.7
Hemicelluloses	19.4	H	6.05	Volatiles	81.4	LHV	18.3
Cellulose	40.9	N	0.47	Ash	1.9		
Lignin	32.7	O	44.73[a]				

[a]By difference

[6]Chapter based on: Mayer Z A, Apfelbacher A, Hornung A (2012) Journal of Analytical and Applied Pyrolysis 94: 170-176. and
Mayer Z A, Apfelbacher A, Hornung A (2012) Journal of Analytical and Applied Pyrolysis 96: 196-202.

7.2. Cation Exchange in Wood

To compare the ion binding properties of wood, acid pre-treated willow was ion-exchanged in the high concentration solutions of $NaNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$ and $Fe(NO_3)_3$. After soaking the acid-washed wood material in the solutions of metal nitrate the samples were washed several times with deionised water until the conductivity of the rinse water matched that of the original deionised water, indicating that unbound metals and salts have been completely removed from the surface of the particles. As the next step, samples were soaked in deionised water and the conductivity was checked regularly and found to be increased for several days until equilibrium was reached.

The measured concentration of heavy metals in wood were found to be the followings: Pb: 18730; Cd: 5374; Fe: 4823; and Zn: 3543 ppm (Figure 14). The concentrations of alkali and alkaline earth metals of Ca, Mg and Na were only 1820, 683 and 378 ppm, respectively, which indicates that these metals bind reversibly and can be removed more easily during water wash.

Similar to anthropogenic soil pollution, ion-exchanged resulted several orders of magnitude higher metal concentrations in plants, compared to plants cultivated in non-contaminated soil. For example willow stems cultivated in contaminated soil can have metal concentrations as high as 18 ppm of lead or 655 ppm of zinc [56, 127] while the relevant metal levels in the uncontaminated raw biomass used in this research were only 1.6 and 51 ppm respectively. The reason why plants from both contaminated and non-contaminated sites show

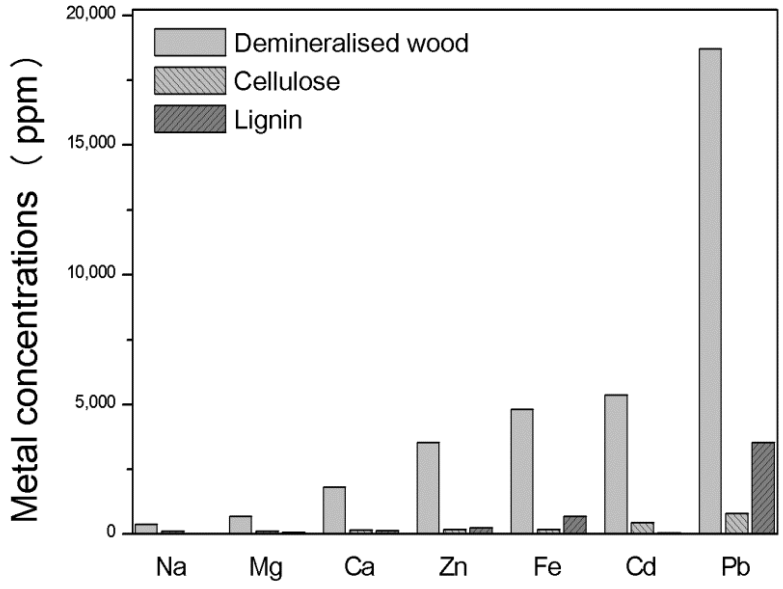


Figure 14 Mass distribution of inorganic elements in ion-exchanged wood, cellulose and lignin

higher zinc levels is that zinc is an essential trace element with good translocation from roots to shoots while lead is a highly toxic metal without biological functions in plants [171, 172].

After repeating the same ion-exchange procedure with pure cellulose, the trend was found similar to wood; lead concentration was the highest (808 ppm) followed by Cd (456 ppm), Fe (193 ppm) and Zn (194 ppm) while concentration of Ca, Na and Mg were 157, 127 and 110 ppm, respectively. Compared to wood and cellulose, lignin shows a different behaviour; when it was ion-exchanged with Cd cation, it resulted in lower metal concentration than lignin loaded with Mg or Ca cations (58, 86 and 145 ppm, respectively) and more lead, iron and zinc ions were bound to lignin (3555, 683, 241 ppm) and less sodium (39 ppm), as compared to pure cellulose.

Both cellulose and lignin had significantly lower metal content after the ion-exchange step than demineralised and ion-exchanged wood. This indicates that the pre-treatment enhanced the metal binding capacity of wood by activating the acidic groups [126]. Even though it was suggested that lignocellulosic materials have higher efficiency to divalent metal ions than to monovalent ions [130], our regression analysis results indicate that the charge of the metal ions had no significant effect on the measured metal concentration in wood, cellulose or lignin (p = 0.7; 0.6 and 0.83, respectively). However, there were several parameters which were not considered in this research like pH of the solvents or the radii of the metal ions.

7.3. Effects of Sample Preparations

7.3.1. Effects of the Pre-treatments on the Thermal Decomposition of the Biomass

The process of the thermal decomposition depends on both the organic and inorganic structure of the biomass and the measured mass loss rate curves from TGA measurements can be interpreted as the independent degradation of the three main organic woody biomass compounds, cellulose, hemicellulose and lignin (see also Figure 10 in **Part I**). In the case of the untreated willow (Figure 15**a)**, the characteristic thermal decomposition temperatures of hemicellulose (at 200-350 °C), cellulose (at 320-400 °C) and the broad peak of lignin with small intensity (at 250-550 °C) can be clearly identified [98].

The untreated and demineralised samples have their initial degradation temperatures at around 200 °C and their cellulose decomposition gave the most intense DTG peaks (Figure 15**a**). While these peaks have similar intensities (i.e. degradation rate), the thermal decomposition temperature of acid-washed sample shifted from 373 °C to 376 °C. Water treatments also shifted the degradation temperatures of cellulose and the acid washed wood to higher temperature regions (curves not shown). These shifts to higher temperatures indicate that the pre-treated cellulose has a higher thermal stability which also explains the reported higher activation energy of the pre-treated wood materials (178.4 kJ/mol) compare to raw wood (89.0

kJ/mol) [144]. Similar shifts were reported during the pyrolysis of water- or acid-demineralised wood and straw. The widely accepted explanation for this phenomenon is the absence of the inorganic promoted cellulose decomposition [107, 131, 137].

The overlapping peaks of the mass loss rate temperature of the solid phase (derivative thermogravimetric curves, DTG) and the peak temperatures of the mass spectrometric total ions curves (TIC) of the forming gases and vapours (Figure 15 **c**) show that the TGA and Py–MS methods can be regarded as complementary analytical techniques. The main observed difference in case of the demineralised samples is the presence of the signal at 650 °C which was identified as levoglucosan (m/z: 60, 57, 73, 43, 56, 70, 45), the main decomposition product of cellulose. The Py–MS peak of levoglucosan appears at a higher temperature than expected and levoglucosan formation

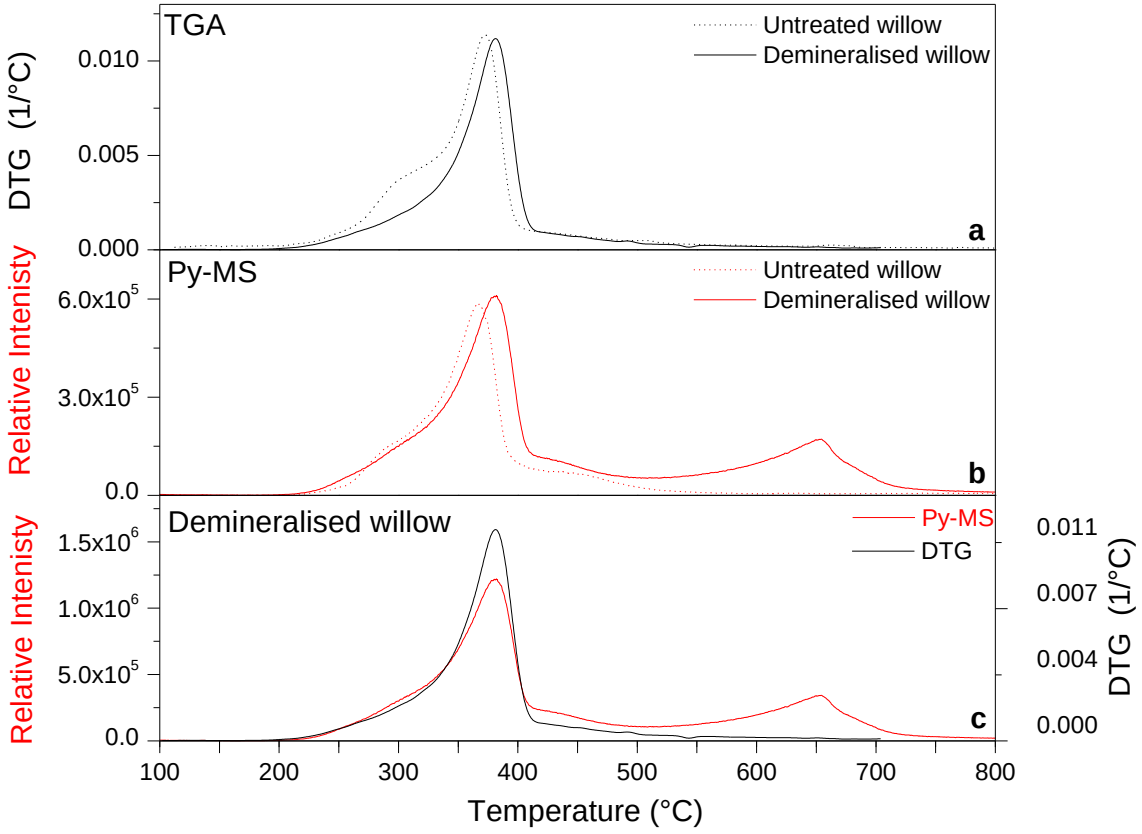


Figure 15 Thermal degradation of demineralised and untreated willow

a) DTG curves of untreated and demineralised willow from TGA measurements; **b**) Total Ion Curves of the evolved gases from Py–MS measurements; **c**) Comparison of the solid phase degradation and evolved gas formation of demineralised willow

was not detected parallel to the degradation of cellulose, which indicates that levoglucosan can be retained in the interface due to its polarity [173].

Another clearly observable difference between the DTG curves of untreated and demineralised wood material (Figure 15**a**) is the absence of the shoulder around 300 °C, related to the degradation of hemicellulose. Fibre analysis results indicate that the aggressive acid wash pre-treatment reduced the hemicellulose content of the sample from 19.4 % to 3.5 % (Figure 16), therefore it is highly probable that the absence of the peak is not an effect of the reduced mineral content of the sample. The fibre analysis results of the raw and pre-treated samples also indicate that the relative content of cellulose remained approximately the same (40.9 % and 42.3 % respectively) while lignin content ostensibly increased from 32.7 % to 51.3 %. As lignin resist acid hydrolysis more than the other biomass compounds, therefore this lignin content was used as a reference value to normalise the results of the fibre analysis. The normalised results show that the absolute cellulose content decreases by 35 %, which indicates that the acid wash significantly reduced not only the hemicellulose but the cellulose content as well.

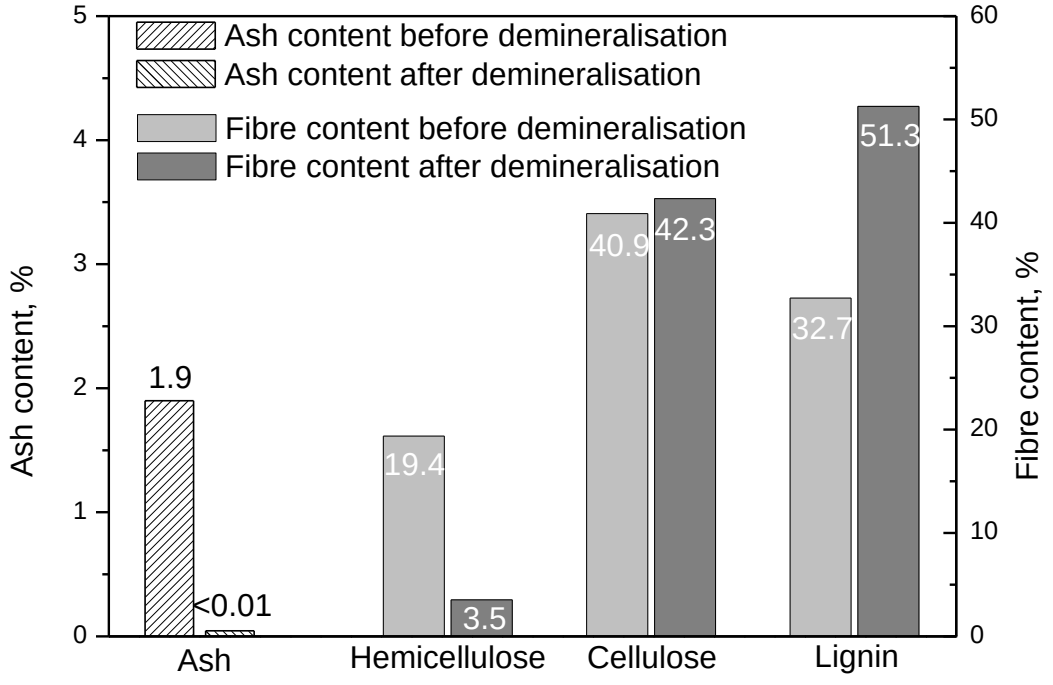


Figure 16 Ash and fibre content of the raw and acid washed biomass

FT–IR measurements were conducted with samples before and after the demineralisation pre-treatment to obtain more information about the structural changes in wood, The FT–IR spectra of untreated willow (**a**), acid washed willow (**b**), water washed willow (**c**) and acid washed and water soaked willow (**d**) are shown on Figure 17.

The first strong broad band in the mid-infrared spectra between 3700 and 3000 cm^{-1} is the sum of overlapping stretching vibrations of O–H functional groups (**I** on Figure 17). The unresolved group of medium weak bands in the region of 2975-2840 cm^{-1} is related to the C–H stretching vibrations of CH_2 and CH_3 groups (**II**). The peak around 1730 cm^{-1} is assigned to the absorption of free carbonyl groups and represents a typical hemicellulose marker (**III**). The next two bands (**IV** and **V**) around 1600 and 1500 cm^{-1} are generaly considered as lignin markers, as this is the region of the skeletal vibrations of aromatic rings (see also Chapter 3.3. in **Part I**).

In the fingerprint region of wood (1500 to 400 cm^{-1}), the spectra contain at least six bands (**VI**) in the C–O stretching region between 1200-950 cm^{-1} that are most probably cellulose-related absorptions [100]. Both acid and water-based treatments seem to sharpen these bands which might indicate changes in the interaction between the C–OH, C–O–C and other functional groups.

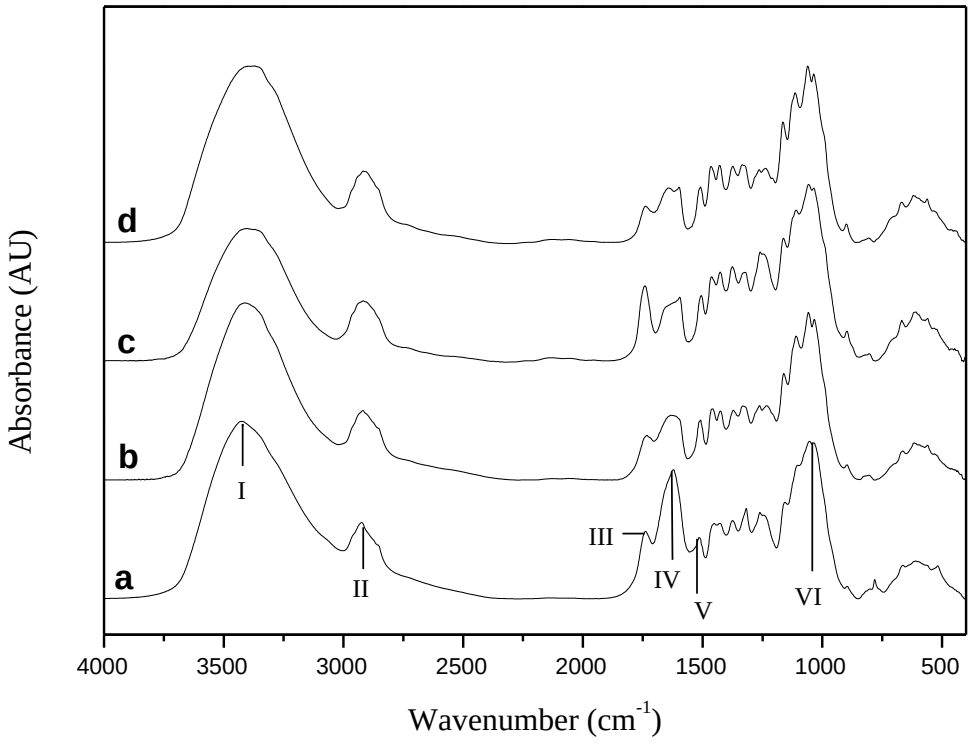


Figure 17 FT–IR spectra of willow

a) Raw willow; **b**) Acid washed willow; **c**) Water washed willow and **d**) Acid washed willow soaked in water

One of the most significant changes in the spectra of the acid washed samples is the decrease of the hemicellulose peak at 1730 cm^{-1} (Figure 17**b** and **d**), which is in agreement with the results of the fiber analysis. The band around 1600 cm^{-1} is normally assigned as a lignin marker [99, 126, 160]; however, it is difficult to exclude the presence of other C=C vibrations or the deformation vibration of water adsorbed into the KBr pellets [174].

Pretreatments also affected the O–H vibrations of wood; the original ratio of the two strong and non-separated bands at 3424 and 3343 cm^{-1} – revealed by curve fitting – was 1 to 0.9. Acid wash decreased band intensity at 3424 cm^{-1} and increased the intensity of the band at 3343 cm^{-1} and lead to a ratio of 1:0.92. The intensity ratio of the same band components in water-washed wood (**c**) and acid-washed wood soaked in water (**d**) changed to 1:0.98 and 1:1, respectively, indicating water related changes in wood structure. As hydrogen-bonded OH groups have lower streching frequencies than free alcohols [97] and stronger H-bonds result in band shifts to lower frequencies [175], we assume that the formation of new or stronger H-bonds led to these changes in the FT–IR spectra. The band at 3343 cm^{-1} with increasing intensity may also be assigned as O–H vibration with interchain H-bonds between the cellulose fibers [100]. The presence of new interchain bonds could explain the increased thermal stability of the demineralised samples during TGA measurements, however, band assignation of FT–IR spectra contains uncertainties due to the presence of water.

Besides of the results from the FT–IR measurements there is another observation whsich does not support the hypothesis that biomass minerals caused the observed shift in the cellulose degradation temperatures; pre-treatment and pyrolysis experiments were repeated with ashless cellulose (Grade 44 Whatman filter paper, purchased from Sigma-Aldrich) and the peak degradation temperature of acid-washed and water-soaked cellulose was also found to be shifted by 8-10 °C to the higher temperature region compared to untreated cellulose (TGA curves not shown).

Even though it seems that the lack of biomass minerals cannot be blamed for the increased thermal stability of cellulose in demineralised wood, the effect of metals on the thermal degradation of biomass is unquestionable and it is the subject of Chapter 7.4.

7.3.2. Effects of the Anions on the Decomposition of Metal Added Biomass

Impregnation is a common method to prepare metal-added samples for pyrolysis experiments. During the impregnation the biomass material is soaked in the salt solution, then the solvent is gradually evaporated [140, 141, 176].

After removing the original mineral content of wood, metal-added samples were prepared in the solution of metal salts. To distinguish between the effects of the metal cations and the anions, lead and zinc salt were used with two different anions, sulphate and nitrate.

Even though chloride salts would have been a self-evident choice, it has already been demonstrated that the presence of chloride and the formation of hydrogen chloride highly effects the biomass decomposition under pyrolytic conditions [131, 138].

The detected difference between the measured DTG curves of the lead nitrate and lead sulphate impregnated samples is the presence of a shoulder around 270 °C (Figure 18**a**). The source of this weight loss might be the biomass degradation catalysed by the melting salt of the chemically non-bonded $Pb(NO_3)_2$. Comparing the weight loss rate curves of zinc sulphate and zinc nitrate impregnated willow (Figure 18**b**), this metal salt related degradation cannot be observed. The zinc sulphate lowered the peak temperature of the impregnated willow ($T_{Zn\text{-}nitrate}$: 374 °C; $T_{Zn\text{-}sulphate}$: 359 °C) and the shape of the DTG curves are markedly different. These changes during the solid phase decomposition indicate that the presence of the zinc sulphate significantly affects the primary degradation mechanism of the wood material. It was also observed that samples prepared with sulphate salt had lower degradation rate compared to the samples prepared with nitrate salts.

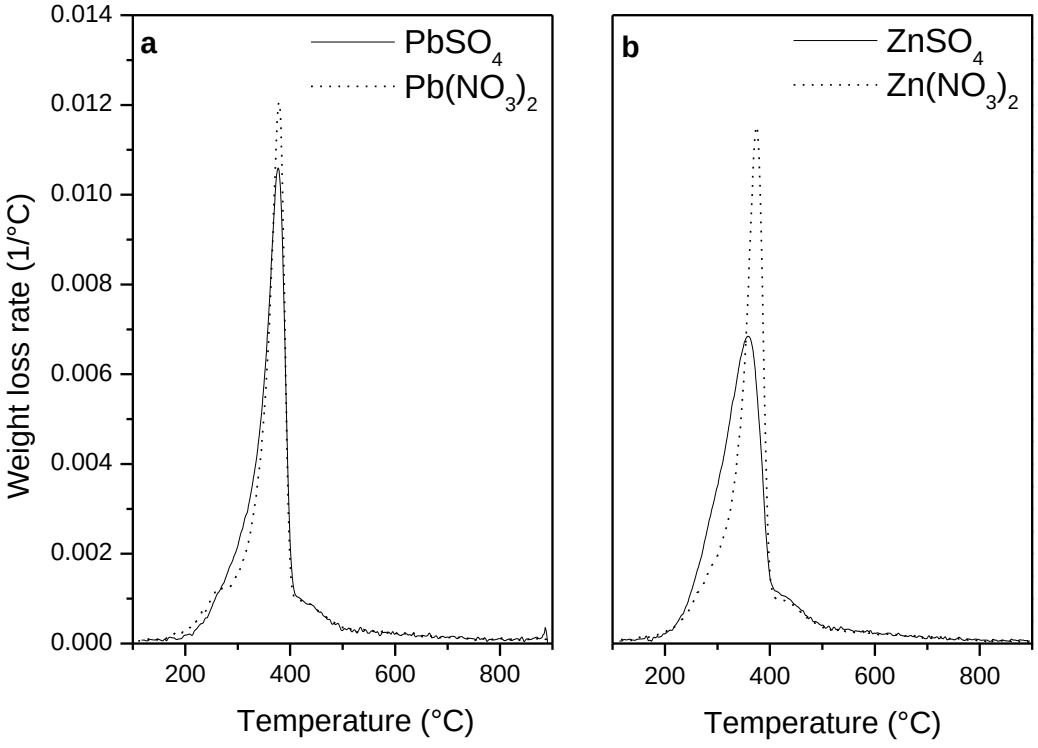


Figure 18 Thermal degradation of impregnated wood

a) Demineralised willow impregnated with lead nitrate and lead sulphate salts;
b) Demineralised willow impregnated with zinc nitrate and zinc sulphate salts

7.3.3. Effects of the Different Metal Addition Methods

To compare the effect of the three different metal addition methods, the demineralised wood was prepared with dry-mixing, impregnation and ion-exchange in a way to have the same lead concentration. This three sample preparation methods represent three different interactions between biomass compounds and added metals; while dry-mixing does not result in any binding between the lignocellulosic material and the added metals, impregnation is mainly physical adsorption on the surface of the biomass particles. The third technique (ion-exchange) aims to simulate the effect of the chemically bonded minerals in wood.

Figure 19 shows the thermal decomposition of the acid-washed willow samples which were dry-mixed, impregnated or ion-exchanged with lead nitrate. Even though the three samples contained lead ion in the same concentration (18730 ppm) their individual sample preparation methods led to characteristically different peak temperatures (dry-mixed: 373 °C; impregnated: 378 °C; ion-exchanged: 382 °C). The DTG curves of both the impregnated and the dry-mixed samples have peaks around 270 °C which might be related to the decomposition

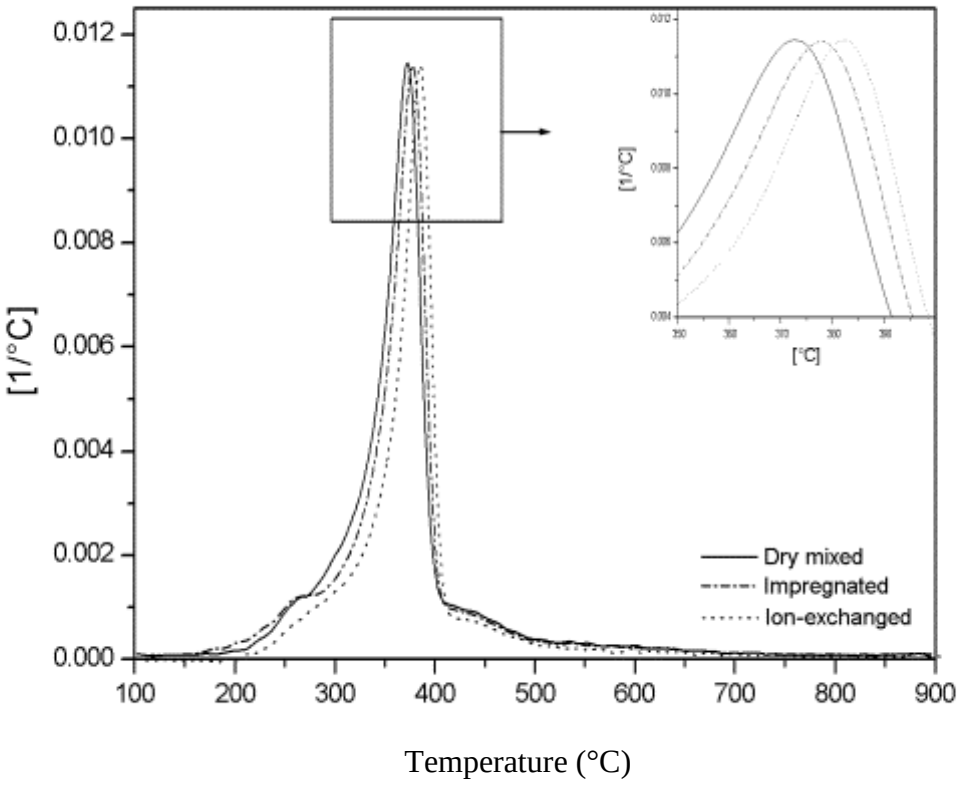


Figure 19 Weight loss rate curves of acid washed willow samples prepared with lead ion

(The DTG curves have been normalised to obtain more comparable results as the ion-exchanged sample gave slightly higher weight loss rate)

of the $Pb(NO_3)_2$ salt. The degradation curve of the ion-exchanged sample lack this peak as nitrate anions and unbound salt have been washed off during the sample preparation.

During the sample preparation process the wood was soaked in water-based metal salt solution, except the dry-mixed sample. For the very same reason control measurements were performed with demineralised wood with and without a water-soaking step. The peak temperature of the demineralised control wood material was 376 °C, which is 3 °C higher than the peak temperature of the wood sample dry-mixed with lead-nitrate ((□) on Figure 19; T_{peak}: 373°C). The other control sample was demineralised then soaked in clean deionised water over a period of 4 days and gave a peak temperature of 381 °C (result not shown), while the peak temperature of the impregnated sample was 378 °C ((- - -) on Figure 19), therefore the observed shift after the metal addition was -3 °C again. The lead exchanged sample ((···) on Figure 19; T_{peak}: 382 °C) gave similar peak temperature as the control mentioned above, therefore lead cation does not appear to have significant catalytic or inhibitor effect in the absence of salt anions.

7.4. Effects of Ash and Metals on the Pyrolytic Behaviour of Wood

7.4.1. Effects of Ash on the Thermal Stability of Wood

The (—) curve on Figure 20**a** shows the weight loss of willow pyrolysis. The peak temperatures of cellulose degradation shifted to higher region when the inorganic compounds of

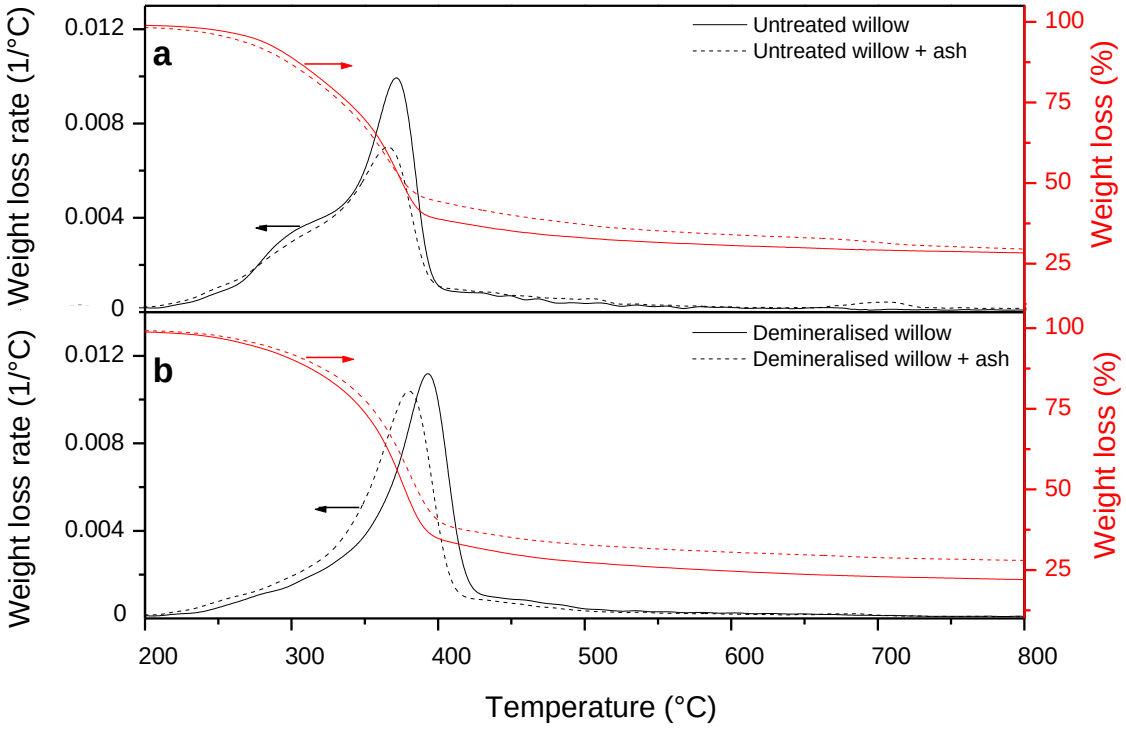


Figure 20 Weight loss curves of wood pyrolysis from TGA measurements

the wood were washed out ((─) demineralised willow, Figure 20**b**) and to lower temperature regions when approximately 2 wt % ash has been added to untreated or demineralised wood ((····) on Figure 20**a** and **b**). The added ash did not seem to change the degradation pattern of hemicellulose or lignin extensively. Another clearly observable difference between the degradation curves of untreated and demineralised wood material is the absence of the hemicellulose related shoulder around 300 °C. Fibre analysis results indicated that the acid wash reduced the hemicellulose content of the sample from 19.4 % to 3.5 % (see also Figure 16 in Chapter 7.3.) therefore the absence of the shoulder was presumably not an effect of the reduced mineral content of the samples.

7.4.2. Thermal Stability of the Metal Added Wood

The ion-exchanged wood was prepared and pyrolysed to investigate the effect of the individual metal ions without the presence of the inherited biomass minerals. When the cations of seven metals (Na, Mg, Ca, Zn, Cd, Pb and Fe(III)) were introduced to willow by ion-exchange, they chemically bonded to the biomass, therefore pyrolysis measurements were possible with the willow in the absence of the metal salt anions. Similarities in the shapes of the weight loss curves (Figure 21) indicate that metals of ion-exchanged wood did not change the main degradation pathways in solid phase, however, some of the added metal ions led to a shift in peak temperatures of cellulose degradation: Iron and zinc seem to catalyse the cellulose degradation, while calcium inhibit it by shifting the peak temperature to higher temperature ranges.

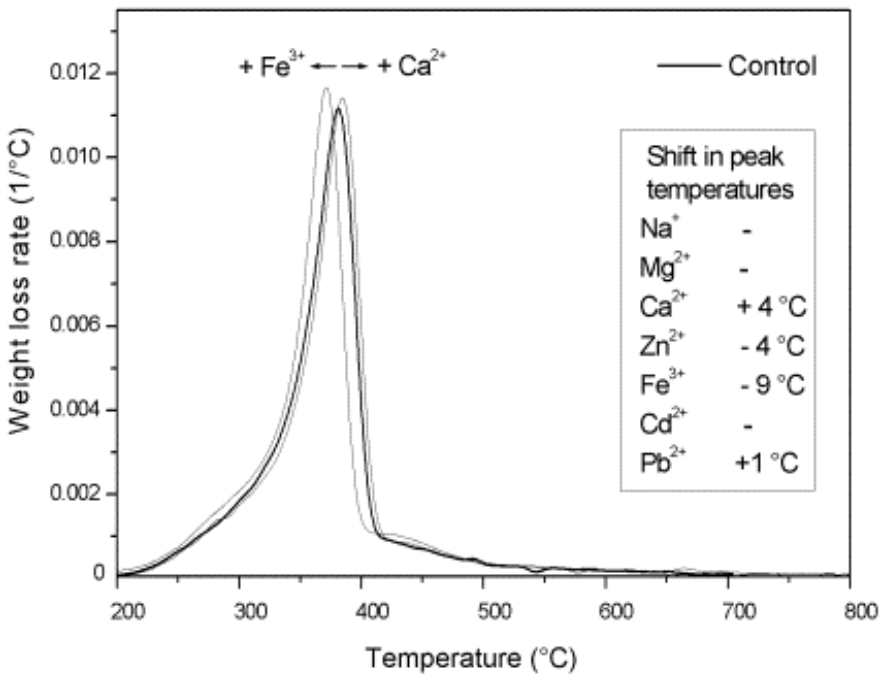


Figure 21 Weight loss curves of ion-exchanged wood pyrolysis from TGA measurements

7.4.3. Biomass Char Yield

Char yield was slightly sensitive to the presence of added ash; the pyrolysis of the untreated willow and willow with added ash yielded approximately 28 % biomass char. The absence of ash in the demineralisation wood dropped the char yield to 21 % and increased back to 27 % when ash was "replaced" by added ash (see also (—) and (····) on Figure 20**b**). There was an extra weight loss peak detected around 700 °C during the pyrolysis of the ash added willow which was followed by CO_2 formation which suggests that ash catalysed the carbon conversion to CO_2 in char.

The pyrolysis of ion-exchanged wood was followed by enhanced char formation, except in case of sodium, where there was a minor decrease from 21 to 20 % (Table 8). Other metals increase char yield up to 28 %. The increase in biomass char yield show similar trend to the initial metal concentrations and statistical results indicate that the measured char yields are not independent from metal concentrations in wood (p=0.04). It was previously suggested that divalent metals can enhance char yield by forming crosslinks [177], however, no significant regression was found between char yield and the charge of the metal ions (p=0.1).

Table 8 Biomass char and levoglucosan yields of wood pyrolysis obtained from TGA and Py–GC–MS measurements

Wood sample	**Char yield** (wt %)	**Levoglucosan yield** (% in vapour phase)
Control	21	88
+ Na	20	29
+ Mg	24	62
+ Ca	25	55
+ Zn	24	56
+ Fe(III)	25	61
+ Cd	25	46
+ Pb	28	41

7.4.4. Levoglucosan Yield

Inorganic compounds affect not only the char and gas formation but also the distribution of compounds forming bio-oil. The most significant difference between the representative chromatograms of willow pyrolysis (Figure 22) is that demineralisation pre-treatment increased the peak area of levoglucosan from 10 to 88 % (see also Figure 15**b** in Chapter 7.3.). Levoglucosan formation has been described as acid-catalysed degradation of cellulose [138, 150] therefore this increase can be explained by the nature of the demineralisation pre-treatment which was performed with HCl.

The highest levoglucosan yield was found in vapour phase (over 90 %) when pure cellulose was pyrolysed (pyrogram not shown). The cellulose-to-levoglucosan conversion decreased when metal ions were added to biomass and the cellulose-to-levoglucosan conversion ranged between 29 % (Na) and 62 % (Mg). When results were tested by regression analysis it was found that metal

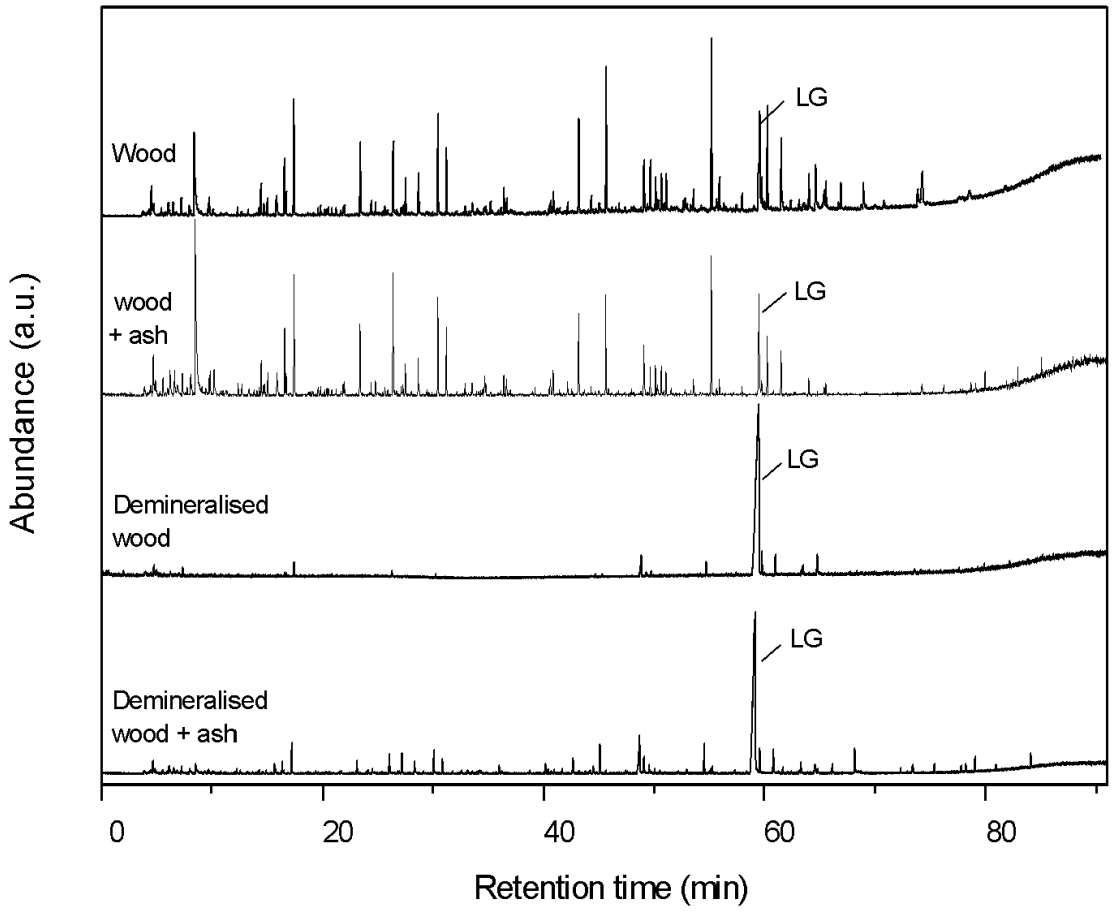


Figure 22 Pyrograms of untreated, pre-treated and ash added willow from Py–GC–MS measurements

concentration has no significant effect on levoglucosan yield (p=0.6), which indicates that metal ions have a selective catalytic or inhibitor effect; The observed levoglucosan yield could be reduced during its primary forming reaction in the presence of inorganic compounds [135]. Furthermore some metals – especially sodium – are known as cracking catalyst of biomass vapours in secondary reactions [178] which can also result in smaller levoglucosan yield [179, 180] in agreement with the results presented in the Table 8.

7.5. Combustion Properties of the Metal- and Ash-enriched Char

Biomass pyrolysis represents the volatilisation and thermal degradation of the organic compounds and biopolymers in inert atmosphere, which leads to the accumulation of the inorganic compounds in char [111, 181]. The effect of inherited and added metals on the burning properties of biomass char was investigated in this research via a series of combustion experiments. Char from demineralised, ash-added and ion-exchanged wood was also prepared and the burning profiles of char samples were compared.

The results of the non-isothermal combustion experiments indicate that thermal behaviour of biomass char in oxidative atmosphere is similar to coal [163-165]; two successive mass loss rate peaks were observed during char combustion of willow (Figure 23**a**) within the temperature range of 270 °C (*initial combustion temperature*) and 637 °C (*burnout temperature, BOT*) with a total conversion (C_{total}) of 88–97 %. The main characteristics of char combustion are presented in Table 9. (See also Appendix V (A) and (B) for the explanation of the abbreviations.)

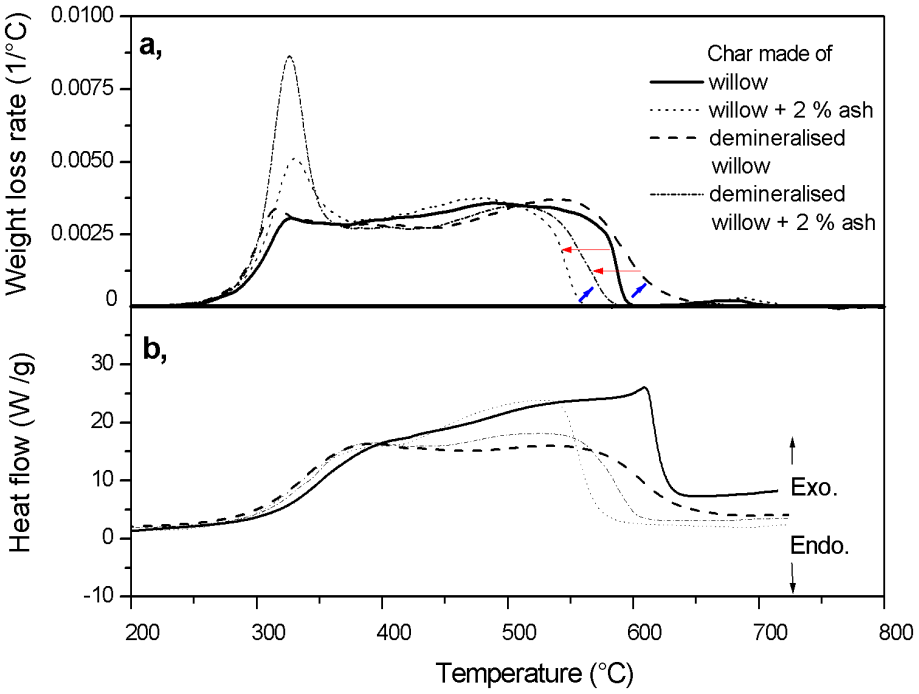


Figure 23 Burning profile of char from TGA–DSC measurements

a) Weight loss rate during combustion; b) Heat released during combustion

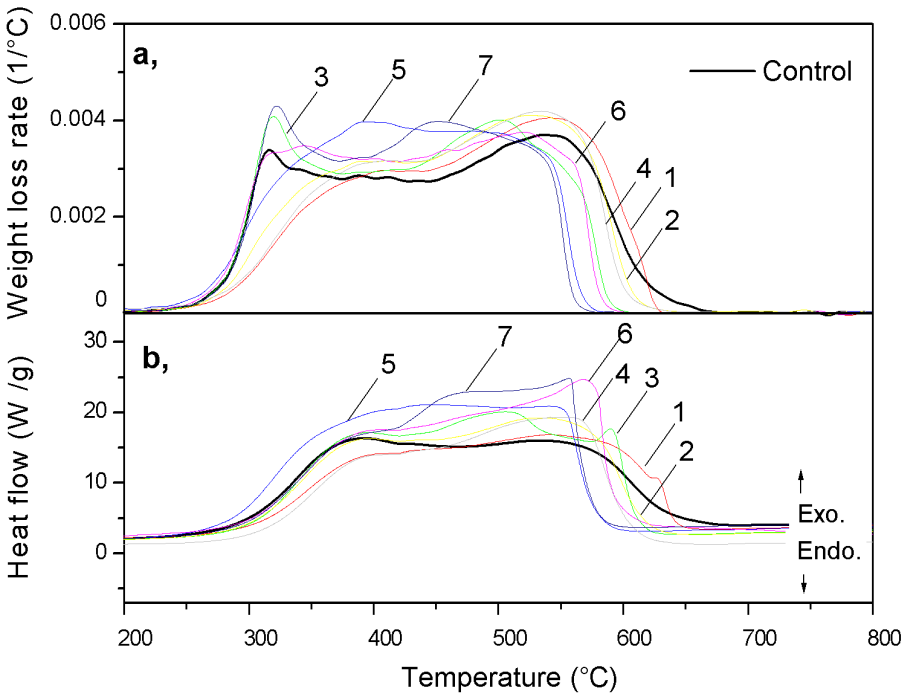


Figure 24 Burning profile of char in the presence of added metals

a) Weight loss rate during combustion; b) Heat released during combustion (Char of willow previously ion-exchanged with **1**, Na^{+}; **2**, Mg^{2+}; **3**, Ca^{2+}; **4**, Zn^{2+}; **5**, Fe^{3+}; **6**, Cd^{+}; **7**, Pb^{2+})

Evolved gas analysis shows that the formation of the detected ions (m/z: 18, H_2O^+ and 44, CO_2^+) followed the patterns of the weight loss curve at lower temperature region with a maximum around 325 °C (Figure 25). C_xH_y fragment ions (e.g. $C_3H_3^+$ and $C_3H_7^+$) were also detected with smaller abundance. TGA measurements with char heated under inert atmosphere also release volatiles between 300 and 400 °C (curves not shown) which indicate that biomass char samples contain organic compounds besides of the pyrogenic carbon. Therefore, the first step of char combustion was identified as the release of these hydrocarbons. Although char samples were prepared on 500 °C where the thermal degradation of the main wood compounds is finished, heat transfer problems during biomass char preparation could lead to incomplete carbonisation. Other possible explanation for the presence of these volatiles is that the longer residence time of gases – as compared to pyrolysis in a constantly purged TGA system – favoured to the repolimerisation of vapours which remained in char [182].

The maximum rate of this weight loss reaction was between 315-325 °C and was followed by the combustion of the released vapours as indicated by the CO_2 and water formation and the detected exothermic peak shown on Figure 23**b**. The shift in the maxima of the weight loss rate and the heat flow peak temperatures can be explained with delays in oxygen diffusion [183].

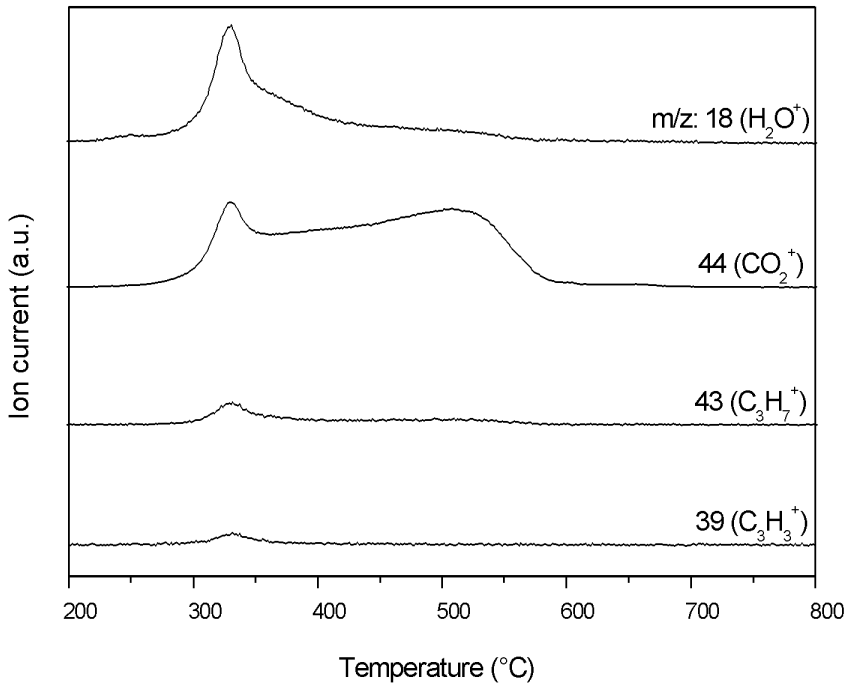


Figure 25 Ion current curves from combustion TG–MS studies of char prepared from demineralised willow in the presence of external ash

The heat flux curves of char combustion have also two regions (Figure 23**b**). Both regions were exothermic with maximum heat flow rates of 16 and 26 Wg^{-1} with slightly varying peak temperatures as compared with the weight loss rate curves.

The first rapid weight loss step of char combustion was followed by a slower reaction. This second reaction is the actual combustion of the carbon rich char, as evidenced by exothermic heat flow and CO_2 formation. Similar to the pyrolysis experiments, the combustion of samples with high ash content have an additional peak around 700 °C (Figure 23**a**); however, as this temperature is over the *BOT*, this change in the solid phase is not related to the carbon content of the char. The ash has other effects on biomass char combustion; while demineralisation delayed the burnout of the char, the added ash shifted *BOT* to lower temperatures (Figure 23**a)**. As the relative ratio of inorganic compounds is increasing during the combustion process it was expected to find more differences around *BOT* in the presence of added ash. The comparison of the shape of the weight loss rate curves in this region demonstrates that solid phase reactions were different and that the inherited ash catalysed char combustion by a different mechanism than the added ash (see also the angular and horizontal

Table 9 Combustion characteristics of the biomass char

	T_{max} [a] (°C)	R_{max} [b] (1/min)	*BOT* (°C)	C_{total} (wt %)	D_i [c] (x 10^{-5})
Willow	485	0.072	597	92	8.63
+ ash	472	0.075	552	88	9.27
Demineralised willow	526	0.074	637	97	8.33
+ ash	473	0.071	584	92	8.45
Ion-exchanged willow					
Control	526	0.074	637	97	8.33
+ Na	561	0.082	626	94	9.27
+ Mg	528	0.082	602	95	9.39
+ Ca	494	0.081	587	91	9.58
+ Zn	534	0.085	600	92	9.45
+ Fe(III)	500	0.075	569	91	9.50
+ Cd	520	0.076	561	95	9.17
+ Pb	446	0.075	554	89	9.25

[a] T_{max}: Peak temperature where rate of weight loss of carbon combustion was maximum

[b] R_{max}: Maximum rate of weight loss corresponds to actual char combustion.
$R_{max} = - dw/dT_{max} \cdot 1/w_0$, where w_0 is the initial weight of the char

[c] D_i: Ignition index, $D_i = R_{max} /(t_{max} \cdot t_{in})$ where t_{in} is the starting time of the initial ignition (approximately 24 min at 270 °C) and t_{max} is the time when the combustion rate was at its maximum (33-37 min).

arrows on Figure 23**a**). This figure demonstrates another significant difference: ash enhances the volatile release of char significantly at the lower temperature range (300-350 °C) of biomass char combustion. It is also known that both the primary formation and secondary reactions of volatiles are sensitive to the presence of inorganic compounds [114, 184] and heterogeneously catalysed oxidation of volatiles can explain this increase in weight loss in the presence of ash [185]. DeGroot et al. [186] also reported the catalytic and inhibiting properties of inorganic additives which effected the oxidation properties of char but not its structure. Therefore it can be concluded that the observed changes are related to the oxidation of the volatiles or char but not to structural changes in the solid phase.

Figure 24 shows the burnout profiles of char prepared from ion-exchanged wood. The weight loss rate curves do not seem to follow a single pattern, which implies the different roles of each metal cations on the combustion of biomass char. However, similarly to the heat flow results of Figure 23**b**, two maxima were observed in the heat release profile (Figure 24**b**) and the figure shows some other similarities to the combustion behaviour of the ash added samples. The similar R_{max} values from the second step of char combustion indicates that the absence or presence of biomass minerals and inorganic compounds do not increase or decrease char reactivity significantly, but the total conversion of the ash and metal added biomass char was found to be lower. When the original ash content was removed and then replaced by added ash, the C_{total} remained the same (92 %) but the *BOT* decreased.

To estimate the actual effect of ash on the ignition performance of biomass char, ignition indices (D_i) [166, 187] were also determined. The char derived from demineralised willow gave the smallest D_i value ($8.33 \cdot 10^{-5}$) and D_i had a maximum when the original ash content of willow was doubled prior to char formation ($9.27 \cdot 10^{-5}$). Ion-exchange also decreased C_{total} and slightly increased R_{max}, and metals shifted *BOT* to lower temperature regions by 11-83 °C. The ignition indices of these char samples increased to 9.17- 9.58 $\cdot 10^{-5}$ compared to the original $8.33 \cdot 10^{-5}$ D_i value of the control char. These results clearly indicate that ash and added metals promote char decomposition and combustion. Based on the assumption that most inorganic compounds accumulate in char [111, 181], statistical calculations suggested that the shifts in *BOT* and the estimated values of C_{total} and D_i were not related to the initial metal concentrations of willow (p = 0.20, 0.16 and 0.22, respectively).

Chapter 8: Conclusions and Recommendations of Part I and II

Chapter 8 contains the most important findings of **Part I** and **II** and it is suggesting steps for further work.

8.1. Conclusions

Nitrogen has always been the "weakest link" in the food chain and agriculture. Without additional nitrogen, the present capacity of Earth's topsoil is not able to satisfy our hunger for biomass for food or energy. Even though wastewater is a valuable source of nitrogen but untreated wastewater causes harmful nitrate leaching into the groundwater and fresh water. Plants cultivated for wastewater treatment can be considered as energy crops and bring land back into economic use.

Wastewater irrigated willow from a bioremediation pilot plot of the Agri-Food & Biosciences Institute was harvested for analysis and bench scale pyrolysis experiments. **Part I** of the present research investigated the effect of pyrolysis temperature on biochar (BC) properties relevant to soil remediation. The analysis followed the nitrogen cycle from energy crop cultivation and wastewater irrigation through the energy conversion process to the use of BC as a soil amendment.

Results of the analysis showed that wastewater irrigation doubled the nitrogen content of the willow compared to the non-wastewater irrigated control. The extra nitrogen in the willow wood was mainly stored in the form of free amino acids (glutamine, arginine, asparagine etc.). During the pyrolysis process nitrogen retention in the liquid product increased from 4 % to 15 % in the organic phase and from 8.6 % to 28 % in the water phase when the highest treatment temperature increased from 410 °C to 810 °C. Nitrogen retention in BC decreased from 81 % to 51 % with increasing temperature (410 °C to 810 °C) but the majority of the wood derived nitrogen still accumulated in the solid BC product. The final nitrogen content of char was not affected by the purging gas of the reactor which indicates that there is no N_2 uptake during or after the pyrolysis process.

The results of the analyses show that although nitrogen assimilated by the wastewater irrigated willow accumulates in the BC it does so in stable heterocyclic compounds which limit the direct fertilisation effect of the BC. The analysis of extractable potassium, phosphorus, calcium, magnesium and total dissolved solids (TDS) showed that the direct nutrient value of char increased with increasing pyrolysis temperature but did not reach high concentration levels by comparison to traditional fertiliser products.

The chemical composition of the biochar is sensitive to the pyrolysis temperature and the thermal degradation of the main wood compounds (cellulose, hemicellulose and lignin) can be identified by FT–IR measurements. These temperature dependent changes in wood and

biochar chemical structure lead directly to changes in the surface and other physicochemical properties of the biochar. Results of characterisation indicated that the willow BC had low surface area (1.4 to 5.4 m2/g), low bulk density (0.15–0.18 g/cm^3) high pH values (7.8–9.4) and high water-holding capacity (1.8 to 4.3 cm^3/g). The estimated half-life of BC prepared at temperatures below 600 °C is 100-1000 years and greater than 1000 years for BC prepared at temperatures above 600 °C. These parameters are highly relevant to soil quality analysis and management.

The temperature dependence of these main BC characteristics offers the ability to design BC for the remediation of specific soil problems - potentially bringing powerful new solutions to soil management.

In **Part II** of the present research a common energy wood (Salix) was characterised, acid washed and metal added in two different metal salt forms (sulphate and nitrate) for analytical scale pyrolysis experiments. Prior to the demineralisation step the fuelwood characteristics of the wood material were determined and both metal content and fibre content were measured before and after the acid wash pre-treatment. Chemical structure changes in wood material were also investigated with FT-IR. As a next step demineralised samples were metal salt added by means of dry-mixing, impregnation and ion-exchange with the same metal ion concentrations. To follow the decomposition of the raw, demineralised and metal added samples and a well-defined pyrolysis heating rate (20 °C/min) was chosen and results obtained from TGA and Py-MS measurements were compared.

Demineralisation pre-treatments have a strong influence on the FT-IR spectra of wood due to its structural changes. Demineralisation with HCl can effectively decrease the mineral content of wood but it also changes its primary polymer structure, decreases the hemicellulose content.

Demineralisation pre-treatment has also increased the thermal stability of cellulose during pyrolysis. The Increased thermal stability of cellulose can be related to the changes in the primary polymer structure (formation of new H-bonds within cellulose) and not to the absence of the inorganic promoted cellulose decomposition.

Sample preparation was also found to be a crucial factor during pyrolysis when metal salts were added to the wood material; dry-mixing, impregnation or ion-exchange influenced the thermal behaviour of wood in different ways; Gravimetric analysis was used to compare the pyrolysis behaviour of samples impregnated with sulphate and nitrate salts of the same metal. Wood prepared with zinc sulphate and zinc nitrate gave markedly different degradation patterns indicating that the anion of the metal salts can

have significant impact on the degradation of impregnated wood. Samples impregnated with lead sulphate and lead nitrate gave less different degradation patterns, however, an extra peak with small intensity was detected. Impregnation is mainly physical adsorption on the particle surface, therefore it is assumed that this weight loss was related to the release of discrete nitrate salt. Similar peak was also observed on the DTG curve of sample dry-mixed with lead nitrate. This peak was expected as dry addition does not lead to the formation of chemical bounds between inorganic salts and the organic phase of wood.

A third sample preparation approach (ion-exchange) was also analysed for differences. Measurements presented in the Thesis were strongly influenced by the pre-treatments of wood, the metal addition methods and the presence of the metal salt anions. As a general conclusion wood material pyrolysed in the presence or absence of metals and minerals must be prepared carefully to gain reliable and comparable results.

Metal added willow was also prepared with 7 different cations by ion-exchange and the thermal stability of the samples was compared by recording their weight loss curves during pyrolysis. Differential scanning calorimetry and thermogravimetry were also used to study the combustion behaviour of char residue of the pyrolysed wood materials. The applied analytical techniques were used successfully to determine changes in fuel properties of wood and biomass and results indicate that cellulose, the main cell wall component of wood, can bind more metals than lignin. The metal binding capacity of wood and its cell wall components are stronger in case of heavy metals like lead and cadmium than for alkali earth and alkaline metals. The presence of Ca, Fe, Pb and Zn ions slightly changed the main degradation peak temperature of cellulose while Na, Mg and Cd ions did not seem to affect the mass loss rate during pyrolysis.

The demineralisation process decreased, while added inorganic compounds increased the char yield during pyrolysis. Char formation was influenced mainly by the quantity and not the quality of the added metal ions.

The relative concentration of levoglucosan in vapour phase was decreased when wood was pyrolysed in the presence of added metals or ash. The results of the regression analysis indicate that levoglucosan yield of wood pyrolysis was mainly affected by the type and not the total amount of the added inorganics.

Weight loss curves of the analytical scale pyrolysis evidenced that the carbonization of willow was completed around 500 °C. However, bench scale pyrolysis

at 500 °C resulted char with high volatile content and char combustion led to the release of these volatiles. The consecutive steps of BC combustion were identified, namely the release and combustion of vapours and the combustion of fixed carbon. Inorganic compounds in BC affected the first step of combustion differently but slightly increased combustion reactivity (rate of weight loss) during the second step of combustion. Both ash and added metals acted as promoters during char combustion by decreasing the burnout temperature and increased the ignition performance of char. The presence of ash also catalysed the carbon conversion to CO_2 during char combustion.

8.2. Contribution to Knowledge

Organic and inorganic nitrogen (N) and other water contaminants are a threat to aquatic eco-systems and human health. The mitigation of these harmful effects is costly when traditional wastewater treatment processes are used.

Some crops, defined as vegetation filters, can reduce the concentration of these contaminants by the uptake of pollutants from wastewater. These crops do not require additional fertilisers to thrive. In addition to providing a low cost alternative for cleaning wastewater vegetation filter crops can be used as energy crops, though so far only in traditional combustion boilers. Use as an energy source is particularly important in rural areas where other fuel sources can be expensive. Also production of solid fuel via traditional forestry can place an unsustainable burden on old-growth forests and cause more general environmental degradation. So using vegetation filters as energy crops can reduce fuel costs and alleviate environmental damage and in this research energy crops from a wastewater treatment plant have been harvested, analysed and used for the first time as pyrolysis feedstock. Bench scale pyrolysis experiments were performed in an in-door constructed reactor, designed and built for the research. The new reactor was proved to be an effective tool to perform wood pyrolysis under well-controlled conditions and collect products for further characterisation. The collected bio-oil has been analysed with a "two-dimensional" GC–MS search algorithm, set up for the research project. The advantage of the "two-dimensional" search algorithm is that it enabled the compound identification by using both the measured MS data and the calculated retention indices simultaneously. This new "two-dimensional" search algorithm provided more reliable compound identification than the two methods separately.

Available studies have focused on a few properties of biochar and used only a narrow range of pyrolysis temperatures. The objective of the second part of the present Thesis is to broaden the scope to include all properties relevant to soil remediation and analyse the effect of a wider range of pyrolysis temperatures. Therefore soil analysis methods have been adapted and used for biochar characterisation.

This research the main techniques to prepare synthetic bioaccumulators have been compared and a new preparation method has been established, and the pyrolytic behaviour of metal-exchanged wood has been investigated in the presence of different metal cations but in the absence of metal salt anions. Coal analysis methods have been also adapted and used in char combustion experiments to analyse the burning profile of biomass char.

8.3. Suggestions for Further Work

Energy conversion applications require economically attractive feedstock, therefore efforts should be made to maximise the utilisation of the sources (land, irrigation water etc.) and to maximise the energy gained from the biomass with a minimum environmental impact. Pyrolysis of wastewater irrigated energy crops offers advantages in both fields, therefore it is an excellent candidate to supply renewable energy, while the soil application of biochar can retain and assimilate the wastewater derived nitrogen back into the environment. Biomass derived char is a known soil amendment and the temperature dependence of the physicochemical properties suggests that engineered biochar can form a new concept of soil management.

Biochar is also a habitat for soil microorganism [85] which can stimulate N_2 fixation and the biological transformation of nitrogen [188-190], therefore short and long term microbial mineralisation studies, nutrient immobilisation tests and laboratory incubation studies should be designed. With these studies the activity of denitrifying enzymes and microorganism in different sets of soil-biochar mixtures could be examined and analysed.

Knowledge on the nitrogen forms and retention (discussed in the Thesis) completed with some new knowledge on microbial nitrogen mineralisation potentials would provide us a good measure of the real nutrient value of char. This could be also the next step towards the soil quality improvement and safe agricultural applications of biochar.

The qualitative and quantitative analyses of the nitrogen compounds presented in the Thesis are also essential for the future estimation on the direct and indirect effects of biochar production and application on the reduction of greenhouse gases like NOx.

With respect to inorganic contaminations, the new ion-exchange method was proved to be an effective sample preparation technique. This sample preparation saturated the wood with organically bonded metals therefore the metal concentration depended on the ion-exchange capacity of the wood. An important direction for further research is to extend both the pyrolysis and combustion experiments of biomass and biomass char samples with varying metal concentrations.

Further work is also required to develop and to scale-up the pyrolysis of metal contaminated wood and to optimise the production of biomass char, bio-oil or the bio-oil derived chemicals.

Bibliography

[1] Thomas C (2010) The Introduction of a Carbon Price and the Use of Agrichar in the Sugarcane Industry. Australian Farm Business Management 7: 43-55.

[2] Accardi-Dey A, Gschwend P M (2001) Assessing the Combined Roles of Natural Organic Matter and Black Carbon as Sorbents in Sediments. Environmental Science & Technology 36: 21-29.

[3] Novotny E H, de Azevedo E R, Bonagamba T J, Cunha T J F, Madari B E, Benites V de M, Hayes M H B (2006) Studies of the Compositions of Humic Acids from Amazonian Dark Earth Soils. Environmental Science & Technology 41: 400-405.

[4] Müller A, Schmidhuber J, Hoogeveen J, Steduto P (2008) Some Insights in the Effect of Growing Bio-Energy Demand on Global Food Security and Natural Resources. Water Policy 10: 83-94.

[5] James S R, Dennell R, Gilbert A S, Lewis H T, Gowlett J, Lynch T F, McGrew W, Peters C R, Pope G G, Stahl A B (1989) Hominid Use of Fire in the Lower and Middle Pleistocene: A Review of the Evidence [and Comments and Replies]. Current Anthropology 30: 1-26.

[6] Antal M J, Grønli M (2003) The Art, Science, and Technology of Charcoal Productionon. Industrial & Engineering Chemistry Research 42: 1619-1640.

[7] Czernik S, Bridgwater A V (2004) Overview of Applications of Biomass Fast Pyrolysis Oil. Energy & Fuels 18: 590-598.

[8] Alexander M (1994) Biodegradation and Bioremediation. San Diego: Academic Press Inc.

[9] Galloway J (2011) A Chronology of Human Understanding of the Nitrogen Cycle 1700-2000. Discussion Meeting on the Global Nitrogen Cycle. The Royal Society, London, 5-6 Dec 2011.

[10] Nicholas I (2003) Nitrogen Uptake in New Zealand short Rotation Crops. Short Rotation Crops for Bioenergy: New Zealand. Crops 1985: 235-240.

[11] Pandey A, Srivastava R K (2010) Role of Dendropower in Wastewater Treatment and Sustaining Economy. Journal of Cleaner Production 18: 1113-1117.

[12] Vasudevan P, Thapliyal A, Srivastava R K, Pandey A, Dastidar M G, Davies P (2010) Fertigation Potential of Domestic Wastewater for Tree Plantations. Journal of Scientific & Industrial Research 69: 146-150.

[13] Roberts K G, Gloy B A, Joseph S, Scott N R, Lehmann J (2009) Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential. Environmental Science & Technology 44: 827-833.

[14] Gaunt J, Cowie A (2009) Greenhouse-gas Accounting and Emissions Trading. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 317-340.

[15] Brownsort P, Carter S, Cook J, Cunningham C, Gaunt J, Hammond J, Ibarrola R, Sims K, Thornley P (2010) An assessment of the Benefits and Issues Associated with the Application of Biochar to Soil. Available from: http://www.biochar.org.uk

[16] Koppolu L, Clements L D (2003) Pyrolysis as a Technique for Separating Heavy Metals from Hyperaccumulators. Part I: Preparation of Synthetic Hyperaccumulator Biomass. Biomass and Bioenergy 24: 69-79.

[17] Sharifi H (1999) A Methodology for Achieving Agility in Manufacturing Organisations: An Introduction. International Journal of Production Economics 62: 7-22.

[18] Backreedy R I, Jones J M, Pourkashanian M, Williams (2003) A Burn-out of Pulverised Coal and Biomass Chars. Fuel 82: 2097-2105.

[19] Henrich E, Bürkle S, Meza-Renken Z I, Rumpel S (1999) Combustion and Gasification Kinetics of Pyrolysis Chars from Waste and Biomass. Journal of Analytical and Applied Pyrolysis 49: 221-241.

[20] Patterson R A (2003) Nitrogen in Wastewater and its Role in Constraining On-site Planning in Future Directions for On-site Systems: Best Management Practice. Proceedings of On-site ’03 Conference. University of New England, Armidale 30 Sept-2 Oct 2003. Published by Lanfax Laboratories Armidale. ISBN 0-9579438-1-4. pp 313-320.

[21] Abeliovich A (1992) Transformations of Ammonia and the Environmental Impact of Nitrifying Bacteria. Biodegradation 3: 255-264.

[22] US Environmental Protection Agency (1985). Ambient Water Quality Criteria for Ammonia. (440/5-85-001) EPA

[23] Oglesby R T, Edmondson W T (1966) Control of Eutrophication. Water Pollution Control Federation 38: 1452-1460.

[24] Knobeloch L, Salna B, Hogan A, Postle J, Anderson H (2000) Blue Babies and Nitrate-Contaminated Well Water. Environmental Health Perspectives 108: 675-678.

[25] L’Hirondel J, L’Hirondel J L (2002) Nitrate and Man: Toxic, Harmless or Beneficial. Wallingford: CABI UK Publishing.

[26] Eriksson E, Auffarth K, Henze M, Ledin A (2002) Characteristics of Grey Wastewater. Urban Water 4: 85-104.

[27] European Commission (1991). Council directive of 21 May 1991 concerning urban waste water treatment. (91/271/EEC) EEC. Available from: http://eur-lex.europa.eu/

[28] US Environmental Protection Agency National Primary Drinking Water Regulations. EPA Available from: http://water.epa.gov/drink/contaminants/

[29] Australian Government National Health and Medical Research Council (1996). Australian Drinking Water Guidelines (ADWG). Available from: http://www.nhmrc.gov.au/

[30] Cooper P, Day M, Thomas V (1994) Process Options for Phosphorus and Nitrogen Removal from Wastewater. Water and Environment 8: 84-92.

[31] Verstraete W, Philips S (1998) Nitrification-Denitrification Processes and Technologies in New Contexts. Environmental Pollution 102: 717-726.

[32] von Sperling M (1996) Comparison Among the Most Frequently Used Systems for Wastewater Treatment in Developing Countries. Water Science and Technology 33: 59-72.

[33] Kivaisi A K (2001) The Potential for Constructed Wetlands for Wastewater Treatment and Reuse in Developing Countries: A Review. Ecological Engineering 16: 545-560.

[34] Corcoran E, C. N, Baker E, Bos R, Osborn, H. S (2010) Sick Water? The Central Role of Wastewater Management in Sustainable Development. A Rapid Response Assessment. United Nations Environment Programme, UN-HABITAT, Birkeland Trykkeri AS, Norway. 2010.

[35] Dixon A M, Butler D, Fewkes A (1999) Guidelines for Greywater Re-use: Health Issues. Journal of the Chartered Institution of Water and Environmental Management 13: 322-326.

[36] Gilde L C, Kester A S, Law J P, Neeley C H, Parmelee D M (1971) A spray Irrigation System for Treatment of Cannery Wastes. Journal of the Water Pollution Control Federation 43: 2011-2025.

[37] Bendixen T W, Hill R D, Dubyne F T, Robeck G G (1969) Cannery Waste Treatment by Spray Irrigation-Runoff. Journal Water Pollution Control Federation 41: 385-391.

[38] Delgado A N, Periago E L, Viqueira F D-F (1995) Vegetated Filter Strips for Wastewater Purification: A Review. Bioresource Technology 51: 13-22.

[39] Bogosian G, Sammons L E, Morris P J L, Oneil J P, Heitkamp M A, Weber D B (1996) Death of the Escherichia Coli K-12 Strain W3110 in Soil and Water. Applied and Environmental Microbiology 62: 4114-4120.

[40] Toze S (1997) Microbial Pathogens in Wastewater. Literature Review for Urban Water Systems Multi-Divisional Research Program. Technical Report 1/97. CSIRO Land and Water, (Australia)

[41] Troeh, F. R.; Thompson, L. M. (2005) Soils and Soil Fertility, Oxford: Wiley-Blackwell

[42] Masclaux-Daubresse C, Daniel-Vedele F, Dechorgnat J, Chardon F, Gaufichon L, Suzuki A (2010) Nitrogen Uptake, Assimilation and Remobilization in Plants: Challenges for Sustainable and Productive Agriculture. Annals of Botany 105: 1141-1157.

[43] Gomez A, Leschber R (1986) Sampling Problems for the Chemical Analysis of Sludge, Soils, and Plants. London and New York: Elsevier Applied Science Publishers.

[44] Vitousek P M, Howarth R W (1991) Nitrogen Limitation on Land and in the Sea: How Can It Occur? Biogeochemistry 13: 87-115.

[45] European Fertilizer Manufacturers' Association. Production of Urea and Urea Ammonium Nitrate. EFMA. Brussels, 2000. Available from: http://www.efma.org

[46] Haber F, Le Rossignol R (1913) Über Die Technische Darstellung Von Ammoniak Aus Den Elementen. Zeitschrift für Elektrochemie und angewandte physikalische Chemie 19: 53-72.

[47] Manchester K L (2002) Man of Destiny: The Life and Work of Fritz Haber. Endeavour 26: 64-69.

[48] Wood S, Cowie, A, A Review of Greenhouse Gas Emission Factors for Fertiliser Production. In For IEA Bioenergy Task 38, International Energy Agency: 2004. Available from: http://www.ieabioenergy-task38.org

[49] International Fertilizer Industry Association Annual Production and International Trade Statistics. In: Series of Statistical Reports on 2007 Productio Capacity, Production and International Trade of Key Fertilizers, Raw Materials and Intermediates. IFA (2008) Paris, France

[50] Jaeglé L, Steinberger L, Martin R V, Chance K (2005) Global Partitioning of NOx Sources Using Satellite Observations: Relative Roles of Fossil Fuel Combustion, Biomass Burning and Soil Emissions. Faraday Discuss. 130: 407-423.

[51] Chen G Z, Miao S Y, Tam N F Y, Wong Y S, Li S H, Lan C Y (1995) Effect of Synthethic Waster on Young Kandelia Candel Plants Growing Under Greenhouse Conditions. Hydrobiologia 295: 263-273.

[52] Mohammad Rusan M J, Hinnawi S, Rousan L (2007) Long Term Effect of Wastewater Irrigation of Forage Crops on Soil and Plant Quality Parameters. Desalination 215: 143-152.

[53] Mohammad Rusan M J, Mazahreh N (2003) Changes in Soil Fertility Parameters in Response to Irrigation of Forage Crops with Secondary Treated Wastewater. Communications in Soil Science and Plant Analysis 34: 1281-1294.

[54] Haynes R, Goh K (1978) Ammonium and Nitrate Nutrition of Plants. Biological Reviews 53: 465-510.

[55] Dickson R (1989) Carbon and Nitrogen Allocation in Trees. Annales des Sciences Forestieres 46: 631-647.

[56] Meers E, Vandecasteele B, Ruttens A, Vangronsveld J, Tack F (2007) Potential of Five Willow Species (Salix Spp.) for Phytoextraction of Heavy Metals. Environmental and Experimental Botany 60: 57-68.

[57] Demirbas A (1997) Calculation of Higher Heating Values of Biomass Fuels. Fuel 76: 431-434.

[58] Sims R E H, Hastings A, Schlamadinger B, Taylor G, Smith P (2006) Energy Crops: Current Status and Future Prospects. Global Change Biology 12: 2054-2076.

[59] Demirbas A (1999) Properties of Charcoal Derived from Hazelnut Shell and the Production of Briquettes Using Pyrolytic Oil. Energy 24: 141-150.

[60] Rose J W, Cooper J R (1977) Technical Data on Fuel. 7th edn London: British National Committee, World Energy Conference.

[61] Thompson D, Brown T D, Beér J M (1972) NOx Formation in Combustion. Combustion and Flame 19: 69-79.

[62] Fenimore C P (1971) Formation of Nitric Oxide in Premixed Hydrocarbon Flames. Symposium (International) on Combustion 13: 373-380.

[63] Kuo K K-Y (1986) Principles of Combustion. New York: Wiley-Interscience

[64] Nelson H F (1976) Nitric-Oxide Formation in combustion. AIAA Journal 14: 1177-1182.

[65] Leonard P A, Plee S L, Mellor A M (1976) Nitric Oxide Formation from Fuel and Atmospheric Nitrogen Combustion. Science and Technology 14: 183-193.

[66] Hayhurst A N, Vince I M (1983) The Origin and Nature of "Prompt" Nitric Oxide in Flames. Combustion and Flame 50: 41-57.

[67] Likens G E, Bormann F H, Johnson N M (1972) Acid Rain. Environment: Science and Policy for Sustainable Development 14: 33-40.

[68] Elrod M J (1999) Greenhouse Warming Potentials from the Infrared Spectroscopy of Atmospheric Gases. Journal of Chemical Education 76: 1702-1705

[69] Pitts J N (1993) Anthropogenic Ozone, Acids and Mutagens: Half a Century of Pandora's NOx. Research on Chemical Intermediates 19: 251-298.

[70] Nussbaumer T (1997) Primary and Secondary Measures for the Reduction of Nitric Oxide Emissions from Biomass Combustion. In: Bridgwater A V, Boocock D G B, editors. Development and Thermochemical Biomass Conversion. London: Chapman and Hall. pp. 1447-1461

[71] Victor N M, Victor D G (2002) Macro Patterns in the Use of Traditional Biomass Fuels. Rural Energy Transitions Conference, jointly convened by PESD and the Tata Energy Research Institute, New Delhi, India, 5-7 Nov 2002.

[72] US Environmental Protection Agency (1982) Air Quality Criteria for Oxides of Nitrogen. (600/8-82-026). EPA

[73] Intergovernmental Panel on Climate Change (2006). Guidelines for National Greenhouse Gas Inventories. IPCC Available from: http://www.ipcc-nggip.iges.or.jp

[74] Hansson K-M, Samuelsson J, Tullin C, Åmand L-E (2004) Formation of HNCO, HCN, and NH_3 from the Pyrolysis of Bark and Nitrogen-Containing Model Compounds. Combustion and Flame 137: 265-277.

[75] Hornung A, Apfelbacher A, Richter F, Schneider D, Schöner J, Seifert H, Tumiatti V, Franchi P, Lenzi F, Haloclean - Intermediate Pyrolysis - Power Generation From Rape, 16th European Biomass Conference & Exhibition, Valencia, Spain, 2008.

[76] Hossain A K, Davies P A (2010) Use of Pyrolysis Oil for CHP Application: Difficulties and Prospects. In: Proceedings of the World Renewable Energy Congress (WRECXI), Abu Dhabi, UAE, 25-30 Sept, pp. 121-126.

[77] Lehmann J, Czimczik C, Laird D, Sohi S (2009) Stability of Biochar in Soil. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 183-206.

[78] Shackley S, Sohi S, Brownsort P, Carter S, Cook J, Cunningham C, Gaunt J, Hammond J, Ibarrola R, Mašek O (2010) An Assessment of the Benefits and Issues Associated with the Application of Biochar to Soil. Department for Environment, Food and Rural Affairs (DEFRA), London.

[79] Novak J M, Lima I, Xing B, Gaskin J W, Steiner C, Das K, Ahmedna M, Rehrah D, Watts D W, Busscher W J (2009) Characterization of Designer Biochar Produced at Different Temperatures and their Effects on a Loamy Sand. Annals of Environmental Science 3: 195-206.

[80] Brewer C E, Schmidt-Rohr K, Satrio J A, Brown R C (2009) Characterization of Biochar from Fast Pyrolysis and Gasification Systems. Environmental Progress & Sustainable Energy 28: 386-396.

[81] Joseph S, Peacocke C, Lehmann J, Munroe P (2009) Developing a Biochar Classification and Test Methods. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 107-126.

[82] Schjønning P, Thomsen I K, Petersen S O, Kristensen K, Christensen B T (2011) Relating Soil Microbial Activity to Water Content and Tillage-Induced Differences in Soil Structure. Geoderma 163: 256–264.

[83] Downie A, Crosky A, Munroe P (2009) Physical Properties of Biochar. Biochar for environmental management. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 13-32.

[84] Liang B L, Solomon J, Kinyangi D, Grossman J, O'Neill J, Skjemstad B, Thies J, Luizão J, Petersen F, Neves J (2006) Black Carbon Increases Cation Exchange Capacity in Soils. Soil Science Society of America 70: 1719-1730.

[85] Thies J E, Rillig M C (2009) Characteristics of Biochar: Biological Properties. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 85-106.

[86] Bridle T, Pritchard D (2004) Energy and Nutrient Recovery from Sewage Sludge via Pyrolysis. Water Science & Technology 50: 169-175.

[87] Mukherjee A, Zimmerman A R, Harris W (2011) Surface Chemistry Variations Among a Series of Laboratory-Produced Biochars. Geoderma 163: 247-255.

[88] American Society for Testing and Materials, 1994. ASTM E 954: Standard Practice for Packaging and Shipping of Laboratory Samples of Refuse-derived Fuel

[89] American Society for Testing and Materials, 2003. ASTM D 6323 – 98: Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities

[90] Kováts E (1958) Gas-Chromatographische Charakterisierung Organischer Verbindungen. Teil 1: Retentionsindices Aliphatischer Halogenide, Alkohole, Aldehyde Und Ketone. Helvetica. Chimica Acta 41:1915-1932

[91] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by McNaught A D, Wilkinson A. Blackwell Scientific Publications, Oxford (1997). ISBN 0-9678550-9-8.doi:10.1351/goldbook.

[92] American Society for Testing and Materials, 2007. ASTM E1755-01(2007): Standard Test Method for Ash in Biomass.

[93] Dugan E, Verhoef A, Robinson S, Sohi S (2010) Bio-Char from Sawdust, Maize Stover and Charcoal: Impact on Water Holding Capacities (WHC) of Three Soils from Ghana. 19th World Congress of Soil Science, Soil Solutions for a Changing World, Brisbane, Australia, 1-6 Aug 2010,

[94] Mehlich A (1978) New Extractant for Soil Test Evaluation of Phosphorus, Potassium, Magnesium, Calcium, Sodium, Manganese and Zinc. Communications in Soil Science and Plant Analysis 9: 477-492.

[95] McTaggart I, Smith K (1993) Estimation of Potentially Mineralisable Nitrogen in Soil by KCl Extraction. Plant and Soil 157: 175-184.

[96] Everett D, Haul R, Moscou L, Pierotti R, Rouquerol J, Siemieniewska T (1985) Reporting Physisorption Data for Gas Solid Systems with Special Reference to the Determination of Surface-Area and Porosity (Recommendations 1984). Pure and Applied Chemistry 57: 603-619.

[97] Socrates G (1980) Infrared Characteristic Group Frequencies. New York: Wiley.

[98] Yang H, Yan R, Chen H, Lee D H, Zheng C (2007) Characteristics of Hemicellulose, Cellulose and Lignin Pyrolysis. Fuel 86: 1781-1788.

[99] Owen N, Thomas D (1989) Infrared Studies of "Hard" and "Soft" Woods. Applied Spectroscopy 43: 451-455.

[100] Maréchal Y, Chanzy H (2000) The Hydrogen Bond Network in Ib Cellulose as Observed by Infrared Spectroscopy. Journal of Molecular Structure 523: 183-196.

[101] Boeriu C G, Bravo D, Gosselink R J A, van Dam J E G (2004) Characterisation of Structure-Dependent Functional Properties of Lignin with Infrared Spectroscopy. Industrial Crops and Products 20: 205-218.

[102] Bodîrlău R, Teacă C (2007) Fourier Transform Infrared Spectroscopy and Thermal Analysis of Lignocellulose Fillers Treated with Organic Anhydrides. Romanal Journal of Physics 54: 93–104.

[103] Schwanninger M, Rodrigues J C, Pereira H, Hinterstoisser B (2004) Effects of Short-time Vibratory Ball Milling on the Shape of FT-IR Spectra of Wood and Cellulose. Vibrational Spectroscopy 36: 23-40.

[104] Bilba K, Ouensanga A (1996) Fourier Transform Infrared Spectroscopic Study of Thermal Degradation of Sugar Cane Bagasse. Journal of Analytical and Applied Pyrolysis 38: 61-73.

[105] Johnsson J E (1994) Formation and Reduction of Nitrogen Oxides in Fluidized-bed Combustion. Fuel 73: 1398-1415.

[106] Bridgwater A V, Meier D, Radlein D (1999) An Overview of Fast Pyrolysis of Biomass. Organic Geochemistry 30: 1479-1493.

[107] Di Blasi C, Branca C, D'Errico G (2000) Degradation Characteristics of Straw and Washed Straw. Thermochimica Acta 364: 133-142.

[108] Lang T, Jensen A D, Jensen P A (2005) Retention of Organic Elements During Solid Fuel Pyrolysis with Emphasis on the Peculiar Behavior of Nitrogen. Energy & Fuels 19: 1631-1643.

[109] Zhu Q, Money S L, Russell A E, Thomas K M (1997) Determination of the Fate of Nitrogen Functionality in Carbonaceous Materials During Pyrolysis and Combustion Using X-Ray Absorption Near Edge Structure Spectroscopy. Langmuir 13: 2149-2157.

[110] Pels J R, Kapteijn F, Moulijn J A, Zhu Q, Thomas K M (1995) Evolution of Nitrogen Functionalities in Carbonaceous Materials During Pyrolysis. Carbon 33: 1641-1653.

[111] Koppolu L, Prasad R, Davis Clements L (2004) Pyrolysis as a Technique for Separating Heavy Metals from Hyperaccumulators. Part III: Pilot-Scale Pyrolysis of Synthetic Hyperaccumulator Biomass. Biomass and Bioenergy 26: 463-472.

[112] Krull E S, Baldock J A, Skjemstad J O, Smernik R J (2009) Characteristics of Biochar: Organo-Chemical Properties. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 53-65.

[113] Spokas K A (2010) Review of the Stability of Biochar in Soils: Predictability of O: C Molar Ratios. Carbon 1: 289-303.

[114] Antal M J, Jr., Várhegyi G (1995) Cellulose Pyrolysis Kinetics: The Current State of Knowledge. Industrial & Engineering Chemistry Research 34: 703-717.

[115] Skodras G, Natas P, Basinas P, Sakellaropoulos G P (2006) Effects of Pyrolysis Temperature, Residence Time on the Reactivity of Clean Coals Produced from Poor Quality Coals. Global NEST Journal 8: 89-94.

[116] Hammes K, Schmidt M (2009) Changes of Biochar in Soil. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 169-182.

[117] Brady N C, Weil R R (2007) The Nature and Properties of Soils, Fourteenth ed. New Jersey: Prentice-Hall

[118] Cetin E, Moghtaderi B, Gupta R, Wall T F (2004) Influence of Pyrolysis Conditions on the Structure and Gasification Reactivity of Biomass Chars. Fuel 83: 2139-2150.

[119] Leeper G W, Uren N C (1993) Soil Science : An Introduction, Fifth ed. Melbourne Carlton, Victoria: University Press.

[120] Baxter L L, Miles T R, Jenkins B M, Milne T, Dayton D, Bryers R W, Oden L L (1998) The Behavior of Inorganic Material in Biomass-Fired Power Boilers: Field and Laboratory Experiences. Fuel Processing Technology 54: 47-78.

[121] Davidsson K O, Stojkova B J, Pettersson J B C (2002) Alkali Emission from Birchwood Particles During Rapid Pyrolysis. Energy & Fuels 16: 1033-1039.

[122] Boman C, Öhman M, Nordin A (2006) Trace Element Enrichment and Behavior in Wood Pellet Production and Combustion Processes. Energy & Fuels 20: 993-1000.

[123] Linak W P, Wendt J O L (1993) Toxic Metal Emissions from Incineration: Mechanisms and Control. Progress in Energy and Combustion Science 19: 145-185.

[124] Porteous A (2001) Energy from Waste Incineration -- a State of the Art Emissions Review with an Emphasis on Public Acceptability. Applied Energy 70: 157-167.

[125] Malkow T (2004) Novel and Innovative Pyrolysis and Gasification Technologies for Energy Efficient and Environmentally Sound MSW Disposal. Waste Management 24: 53-79.

[126] Gaballah I, Kilbertus G (1998) Recovery of Heavy Metal Ions through Decontamination of Synthetic Solutions and Industrial Effluents Using Modified Barks. Journal of Geochemical Exploration 62: 241-286.

[127] Lievens C, Carleer R, Cornelissen T, Yperman J (2009) Fast Pyrolysis of Heavy Metal Contaminated Willow: Influence of the Plant Part. Fuel 88: 1417-1425.

[128] Stals M, Carleer R, Reggers G, Schreurs S, Yperman J (2010) Flash Pyrolysis of Heavy Metal Contaminated Hardwoods from Phytoremediation: Characterisation of Biomass, Pyrolysis Oil and Char/Ash Fraction. Journal of Analytical and Applied Pyrolysis 89: 22-29.

[129] Williams P T, Horne P A (1994) The Role of Metal Salts in the Pyrolysis of Biomass. Renewable Energy 4: 1-13.

[130] Kleen M, Gellerstedt G (1995) Influence of Inorganic Species on the Formation of Polysaccharide and Lignin Degradation Products in the Analytical Pyrolysis of Pulps. Journal of Analytical and Applied Pyrolysis 35: 15-41.

[131] Müller-Hagedorn M, Bockhorn H, Krebs L, Müller U (2003) A Comparative Kinetic Study on the Pyrolysis of Three Different Wood Species. Journal of Analytical and Applied Pyrolysis 68-69: 231-249.

[132] Jensen A, Dam-Johansen K, Wójtowicz M A, Serio M A (1998) TG-FTIR Study of the Influence of Potassium Chloride on Wheat Straw Pyrolysis. Energy & Fuels 12: 929-938.

[133] Várhegyi G, Antal M J, Jakab E, Szabó P (1997) Kinetic Modeling of Biomass Pyrolysis. Journal of Analytical and Applied Pyrolysis 42: 73-87.

[134] Alén R, Kuoppala E, Oesch P (1996) Formation of the Main Degradation Compound Groups from Wood and its Components During Pyrolysis. Journal of Analytical and Applied Pyrolysis 36: 137-148.

[135] Eom I-Y, Kim K-H, Kim J-Y, Lee S-M, Yeo H-M, Choi I-G, Choi J-W (2011) Characterization of Primary Thermal Degradation Features of Lignocellulosic Biomass After Removal of Inorganic Metals by Diverse Solvents. Bioresource Technology 102: 3437-3444.

[136] Olsson J G, Jaglid U, Pettersson J B C, Hald P (1997) Alkali Metal Emission During Pyrolysis of Biomass. Energy & Fuels 11: 779-784.

[137] Yang H, Yan R, Chen H, Zheng C, Lee D H, Liang D T (2006) Influence of Mineral Matter on Pyrolysis of Palm Oil Wastes. Combustion and Flame 146: 605-611.

[138] Shafizadeh F, Furneaux R H, Cochran T G, Scholl J P, Sakai Y (1979) Production of Levoglucosan and Glucose from Pyrolysis of Cellulosic Materials. Journal of Applied Polymer Science 23: 3525-3539.

[139] Raveendran K, Ganesh A, Khilar K C (1995) Influence of Mineral Matter on Biomass Pyrolysis Characteristics. Fuel 74: 1812-1822.

[140] Koppolu L, Agblevor F A, Clements L D (2003) Pyrolysis as a Technique for Separating Heavy Metals from Hyperaccumulators. Part II: Lab-Scale Pyrolysis of Synthetic Hyperaccumulator Biomass. Biomass and Bioenergy 25: 651-663.

[141] Khelfa A, Finqueneisel G, Auber M, Weber J V (2008) Influence of Some Minerals on the Cellulose Thermal Degradation Mechanisms - Thermogravimetic and Pyrolysis-Mass Spectrometry Studies. Journal Thermal Analysis and Calorimetry 92: 795-799.

[142] Keown D M, Favas G, Hayashi J I, Li C Z (2005) Volatilisation of Alkali and Alkaline Earth Metallic Species During the Pyrolysis of Biomass: Differences Between Sugar Cane Bagasse and Cane Trash. Bioresource Technology 96: 1570-1577.

[143] Yang H, Yan R, Chen H, Zheng C, Lee D H, Liang D T (2006) In-depth Investigation of Biomass Pyrolysis Based on Three Major Components: Hemicellulose, Cellulose and Lignin. Energy & Fuels 20: 388-393.

[144] Nowakowski D J, Jones J M, Brydson R M D, Ross A B (2007) Potassium Catalysis in the Pyrolysis Behaviour of Short Rotation Willow Coppice. Fuel 86: 2389-2402.

[145] Saghir M (2009) Co-Combustion of Biomass and Biochar. MSc Thesis, Aston University, Birmingham, UK

[146] Wornat M J, Hurt R H, Yang N Y C, Headley T J (1995) Structural and Compositional Transformations of Biomass Chars During Combustion. Combustion and Flame 100: 131-143.

[147] Janse A M C, de Jonge H G, Prins W, van Swaaij W P M (1998) Combustion Kinetics of Char Obtained by Flash Pyrolysis of Pine Wood. Industrial & Engineering Chemistry Research 37: 3909-3918.

[148] Jones J, Williams A, Darvell L, Nawaz M, Baxter X (2004) The Role of Metals in Biomass Pyrolysis, Char Formation and Char Properties. In: Science in Thermal and Chemical Biomass Conversion, Sept 2004, Victoria, Canada

[149] Jones J, Darvell L, Pourkashanian M, Williams A (2005) The Role of Metals in Biomass Char Combustion. In: Proceedings of the European Combustion Meeting, 2005, Louvain-la-Neuve.

[150] Lakshmanan C M, Hoelscher H E (1970) Production of Levoglucosan by Pyrolysis of Carbohydrates. Pyrolysis in Hot Inert Gas Stream. Product R&D 9: 57-59.

[151] Patwardhan P R, Satrio J A, Brown R C, Shanks B H (2009) Product Distribution from Fast Pyrolysis of Glucose-Based Carbohydrates. Journal of Analytical and Applied Pyrolysis 86: 323-330.

[152] Scott D S, Piskorz J, Radlein D (1994) Production of Levoglucosan as an Industrial Chemical. In: Witczak E J, editor. Levoglucosenone and Levoglucosans: Chemistry and Applications. Washington: ATL Press. pp. 179–188.

[153] Zhuang X L, Zhang H X, Yang J Z, Qi H Y (2001) Preparation of Levoglucosan by Pyrolysis of Cellulose and its Citric Acid Fermentation. Bioresource Technology 79: 63-66.

[154] Helle S, Bennett N M, Lau K, Matsui J H, Duff S J B (2007) A Kinetic Model for Production of Glucose by Hydrolysis of Levoglucosan and Cellobiosan from Pyrolysis Oil. Carbohydrate Research 342: 2365-2370.

[155] Richards G N, Zheng G (1991) Influence of Metal Ions and of Salts on Products from Pyrolysis of Wood: Applications to Thermochemical Processing of Newsprint and Biomass. Journal of Analytical and Applied Pyrolysis 21: 133-146.

[156] British Standards Institute, 2009. BS EN 15148: Solid Biofuels — Determination of the Content of Volatile Matter. London: British Standards Institute

[157] British Standards Institute, 2009. BS EN 14775: Solid Biofuels — Determination of Ash Content. London: British Standards Institute

[158] Goering H K, Van Soest P J (1970) Forage Fiber Analysis (Apparatus, Reagents, Procedures and Some Application). Washington DC: Research Service, U.S. Department of Agriculture (ARS USDA)

[159] Mertens D R (2002) Gravimetric Determination of Amylase-Treated Neutral Detergent Fiber in Feeds with Refluxing in Beakers or Crucibles: Collaborative Study. Journal of AOAC International 85: 1217-1240.

[160] Pandey K K (1999) A Study of Chemical Structure of Soft and Hardwood and Wood Polymers by FTIR Spectroscopy. Journal of Applied Polymer Science 71: 1969-1975.

[161] Nowakowski D J, Jones J M (2008) Uncatalysed and Potassium-Catalysed Pyrolysis of the Cell-Wall Constituents of Biomass and their Model Compounds. Journal of Analytical and Applied Pyrolysis 83: 12-25.

[162] Faix O, Fortmann I, Bremer J, Meier D (1991) Thermal Degradation Products of Wood. European Journal of Wood and Wood Products 49: 213-219.

[163] Cumming J W, McLaughlin J (1982) The Thermogravimetric Behaviour of Coal. Thermochimica Acta 57: 253-272.

[164] Smith S E, Neavel R C, Hippo E J, Miller R N (1981) DTGA Combustion of Coals in the Exxon Coal Library. Fuel 60: 458-462.

[165] Serageldin M, Pan W P (1984) Coal Analysis Using Thermogravimetry. Thermochimica Acta 76: 145-160.

[166] Sahu S G, Sarkar P, Chakraborty N, Adak A K (2010) Thermogravimetric Assessment of Combustion Characteristics of Blends of a Coal with Different Biomass Chars. Fuel Processing Technology 91: 369-378.

[167] Phusunti N (2012) Pyrolytic and Kinetic Study of *Chlorella vulgaris* Under Isothermal and Non-isothermal Conditions. PhD Thesis, Aston University, Birmingham, UK

[168] Pulford I D, Watson C (2003) Phytoremediation of Heavy Metal-Contaminated Land by Trees-A Review. Environment International 29: 529-540.

[169] Mleczek M, Kaczmarek Z, Magdziak Z, Golinski P K (2010) Hydroponic Estimation of Heavy Metal Accumulation by Different Genotypes of Salix. Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances & Environmental Engineering 45: 569-578.

[170] Bayley C, Rose G R F (1960) Metal-Organic Complexes Formed During the Treatment of Wood with Metal Salts. Nature 185: 313-314.

[171] Huang J W, Chen J, Berti W R, Cunningham S D (1997) Phytoremediation of Lead-Contaminated Soils: Role of Synthetic Chelates in Lead Phytoextraction. Environmental Science & Technology 31: 800-805.

[172] Hacisalihoglu G, Kochian L V (2003) How Do Some Plants Tolerate Low Levels of Soil Zinc? Mechanisms of Zinc Efficiency in Crop Plants. New Phytologist 159: 341-350.

[173] Fabbri D, Chiavari G, Prati S, Vassura I, Vangelista M (2002) Gas Chromatography/Mass Spectrometric Characterisation of Pyrolysis/Silylation Products of Glucose and Cellulose. Rapid Communications in Mass Spectrometry 16: 2349-2355.

[174] Malhotra V M, Jasty S, Mu R (1989) FT-IR Spectra of Water in Microporous KBr Pellets and Water's Desorption Kinetics. Applied Spectroscopy. 43: 638-645.

[175] Pimentel G C, McClellan A L (1960) The Hydrogen Bond. San Francisco and London: W. H. Freeman And Company.

[176] Szabó P, Várhegyi G, Till F, Faix O (1996) Thermogravimetric/Mass Spectrometric Characterization of Two Energy Crops, Arundo Donax and Miscanthus Sinensis. Journal of Analytical and Applied Pyrolysis 36: 179-190.

[177] Wornat M J, Nelson P F (1992) Effects of Ion-Exchanged Calcium on Brown Coal Tar Composition as Determined by Fourier Transform Infrared Spectroscopy. Energy & Fuels 6: 136-142.

[178] Nik-Azar M, Hajaligol M R, Sohrabi M, Dabir B (1997) Mineral Matter Effects in Rapid Pyrolysis of Beech Wood. Fuel Processing Technology 51: 7-17.

[179] Pattiya A, Titiloye J O, Bridgwater A V (2008) Fast Pyrolysis of Cassava Rhizome in the Presence of Catalysts. Journal of Analytical and Applied Pyrolysis 81: 72-79.

[180] Patwardhan P R, Satrio J A, Brown R C, Shanks B H (2010) Influence of Inorganic Salts on the Primary Pyrolysis Products of Cellulose. Bioresource Technology 101: 4646-4655.

[181] Lievens C, Yperman J, Cornelissen T, Carleer R (2008) Study of the Potential Valorisation of Heavy Metal Contaminated Biomass via Phytoremediation by Fast Pyrolysis: Part II: Characterisation of the Liquid and Gaseous Fraction as a Function of the Temperature. Fuel 87: 1906-1916.

[182] Lewellen P C, Peters W A, Howard J B (1977) Cellulose Pyrolysis Kinetics and Char Formation Mechanism. Symposium (International) on Combustion 16: 1471-1480.

[183] Otero V, Pollock S, Finkelstein N (2010) American Journal of Physics 78: 1218-1224

[184] Zaror C A, Hutchings I S, Pyle D L, Stiles H N, Kandiyoti R (1985) Secondary Char Formation in the Catalytic Pyrolysis of Biomass. Fuel 64: 990-994.

[185] Löffler G, Wargadalam V J, Winter F (2002) Catalytic Effect of Biomass Ash on CO, CH_4 and HCN Oxidation under Fluidised Bed Combustor Conditions. Fuel 81: 711-717.

[186] DeGroot W F, Shafizadeh F (1983) Influence of Inorganic Additives on Oxygen Chemisorption on Cellulosic Chars. Carbon 21: 61-67.

[187] Li X-G, Ma B-G, Xu L, Hu Z-W, Wang X-G (2006) Thermogravimetric Analysis of the Co-Combustion of the Blends with High Ash Coal and Waste Tyres. Thermochimica Acta 441: 79-83.

[188] Sohi S P, Krull E, Lopez-Capel E, Bol R (2010) A Review of Biochar and its Use and Function in Soil. Advances in Agronomy 105: 47-82.

[189] Lehmann J, da Silva J P, Steiner C, Nehls T, Zech W, Glaser B (2003) Nutrient Availability and Leaching in an Archaeological Anthrosol and a Ferralsol of the Central Amazon Basin: Fertilizer, Manure and Charcoal Amendments. Plant and Soil 249: 343-357.

[190] DeLuca T H, MacKenzie M D, Gundale M J (2009) Biochar Effects on Soil Nutrient Transformations. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan. pp. 251-270.

List of Publications

Part I:

- Mayer Z A, Apfelbacher A, Hornung A (2011) Nitrogen Cycle of Effluent-Irrigated Energy Crop Plantations: From Wastewater Treatment to the Thermochemical Conversion Processes. Journal of Scientific and Industrial Research 70: 675-682.
- Mayer Z A, Apfelbacher A, Hornung A: Efforts to Curb NOx from Greenhouse Gases by the Application of Energy Crops and Vegetation Filters. In: B. R. Singh, editor. Global Warming (ISBN 979-953-307-820-4) InTech.
- Mayer Z A, Eltom Y, Stennett D, Schröder E, Apfelbacher A, Hornung A: Characterisation of Engineered Biochar for Soil Management. Submitted to the Environmental Progress & Sustainable Energy (Paper under review. Manuscript number: EP-12-086)

Part II:

- Mayer Z A, Apfelbacher A, Hornung A (2012) Effect of Sample Preparation on the Thermal Degradation of Metal-Added Biomass. Journal of Analytical and Applied Pyrolysis 94: 170-176.
- Mayer Z A, Apfelbacher A, Hornung A (2012) A Comparative Study on the Pyrolysis of Metal- and Ash-enriched Wood and the Combustion Properties of the Gained Char. Journal of Analytical and Applied Pyrolysis 96: 196-202.

Appendices

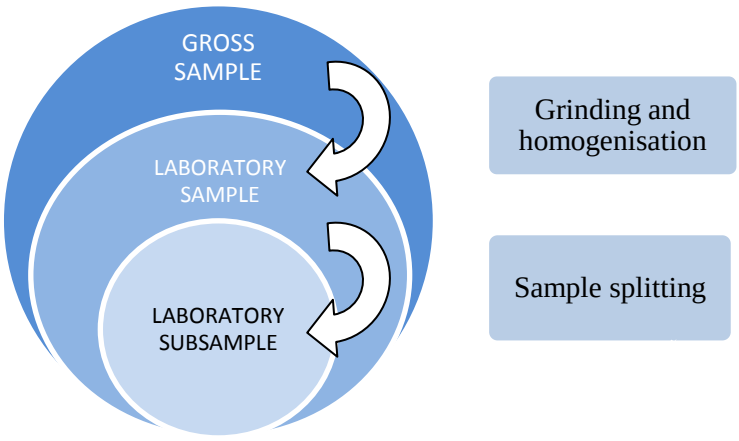
Appendix I Quality assurance in sampling and in laboratory subsampling

I/1. Problem Statement

The aim of sampling is to collect representative samples from the wood resource to estimate some physicochemical properties of the larger population. However, in analytical chemistry improper sampling and sample preparation are significant sources of experimental errors. For this reason a protocol has been outlined to minimise this error and to ensure that the samples represent the original resource.

I/2. Sample preparation for instrumental measurements

To obtain representative samples the collected plant material was grinded and homogenised. Before any physicochemical characterisation measurements the sample bulk was reduced from the original size and *laboratory subsamples* were composed from the *gross samples* and *laboratory samples.*



where the *gross sample* (or composite sample) was composed of a number of shredded tree samples of equal size on which neither any reduction nor division has been performed.

Laboratory sample was a representative portion of the gross sample received by the laboratory for analysis.

Laboratory subsample (or specimen) was collected in such a manner that it reflected the properties of the laboratory sample from which it was collected.

Appendix II Fuelwood characteristics of willow used in Part I

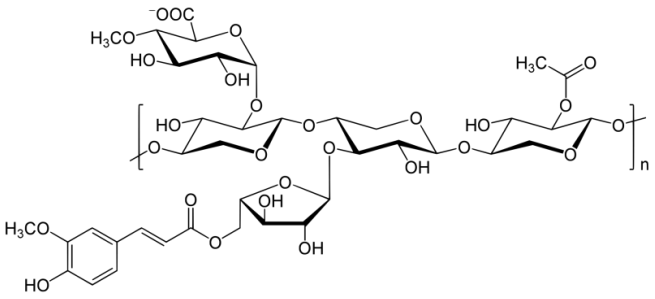
Table 10 Results of the proximate analysis

Proximate Analysis	**Fixed Carbon**	**Volatiles**	**Ash**
	wt %	wt %	wt %
Control	14.5	83.4	2.1
Wastewater irrigated willow	15.3	82.6	2.1

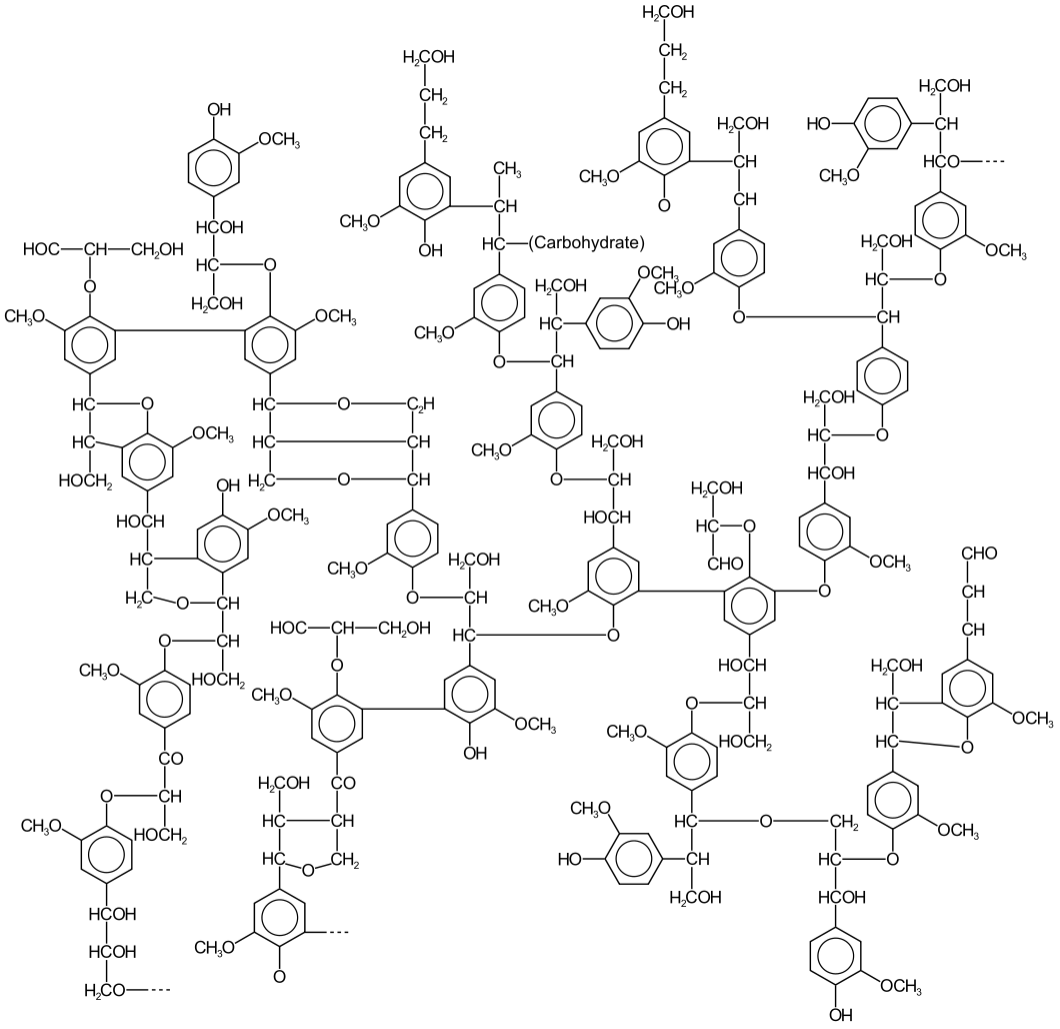
Table 11 Energy content of the willow

Energy Content	**HHV**	**LHV**
	MJ/kg	MJ/kg
Control	19.2	17.9
Wastewater irrigated willow	19.1	17.8

Appendix III Scheme of hemicellulose and lignin structures



Scheme 5 Xylan, the primary hemicellulose component



Scheme 6 The structure of lignin

Appendix IV Biomass characterisation methods of Part I and II

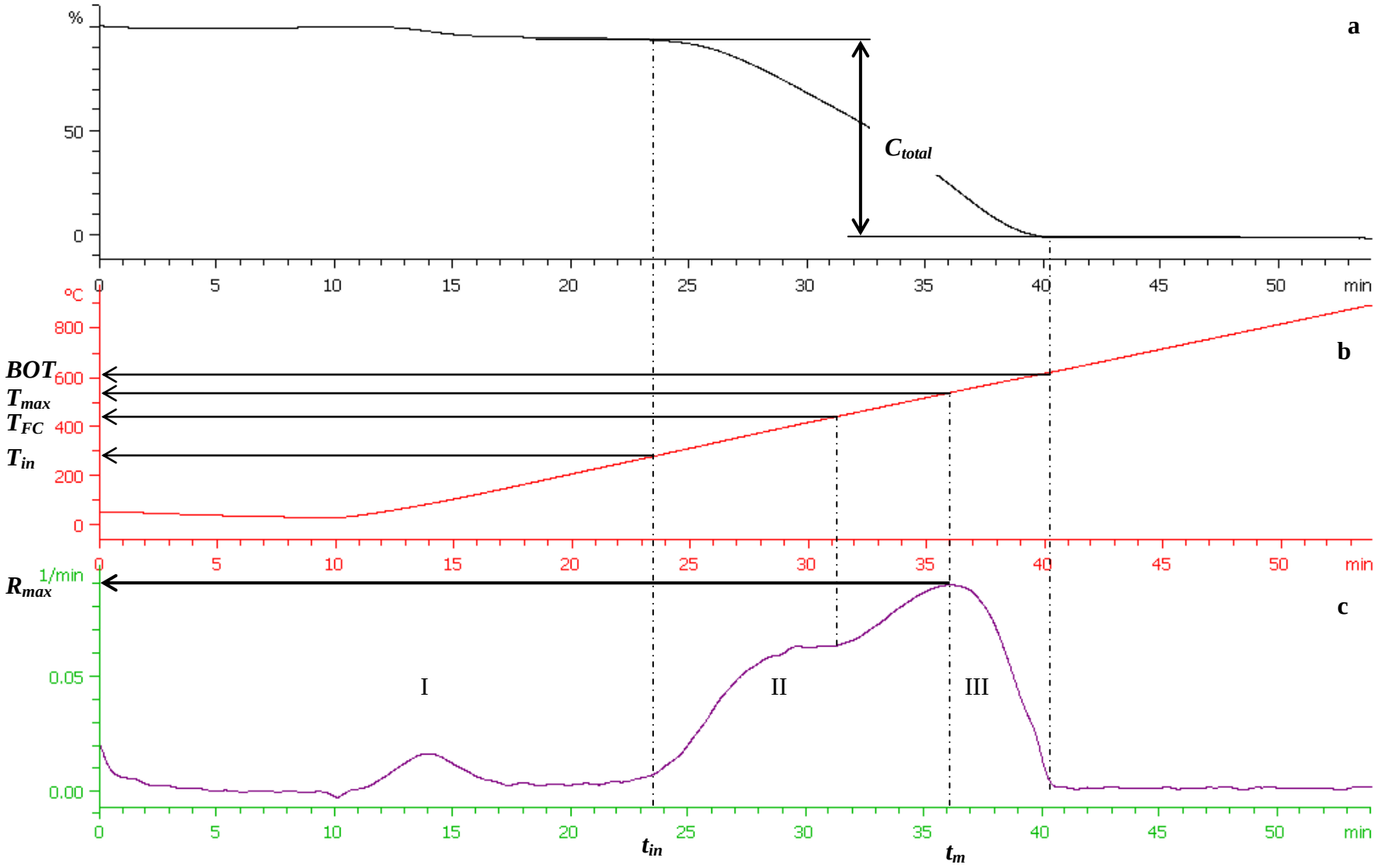
Table 12 List of the wood characterisation methods (Part I)

Sample preparation	Method	References
Preparing gross samples and laboratory samples	ASTM E 954-94 ASTM D 6323-98	[88, 89] and Appendix I
Proximate analysis (moisture, volatile matter, fixed carbon and ash content)	ASTM E 1755-01	[92] and Chapter 3.3.2.
Ultimate analysis (elemental composition, C, H, N and O content)	Method developed by an external laboratory (Medac Ltd)	Chapter 3.3.2.
Carbon and nitrogen functionalities in wood	Method developed by Dr. Shi (Aston University)	Chapter 3.3.4.
Thermogravimetric analysis	Method developed by Mayer et al.	Chapter 3.3.3.

Table 13 List of the wood characterisation methods (Part II)

Sample preparation	Method	References
Wood fibre analysis (hemicellulose, cellulose, lignin content)	FOSS Application Notes 3804 and 3805	[158,159] and Chapter 6.2.3.
Calorimetry (higher and lower heating value measurements)	Parr application notes No. 207M	Chapter 6.2.4.
Fourier Transform–Infrared Spectroscopy	Method developed by Mayer et al.	Chapter 6.2.5.

Appendix V Typical burning profile of the biomass char (A)



Appendix V Typical burning profile of the biomass char (B)

a) Weight loss curve of char combustion (% vs time) where
C_{total} shows the total conversion of the biomass char.

b) Temperature profile of the TGA combustion program (T vs time) where
T_{in} is the initial combustion temperature
T_{max} is the peak temperature where rate of weight loss of carbon combustion is maximum,
T_{FC} is the temperature where the combustion of the fixed carbon starts,
BOT is the burnout temperature of the biomass char.

c) Derivative curve of weight loss (1/min vs time) where
I shows the loss of inherent moisture,
II shows the release of the volatiles,
III shows the combustion of fixed carbon,
R_{max} is the maximum rate of weight loss corresponds to actual char combustion.